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NEUTRADESULFATING TREATMENT PROCESS FOR ACID MINE DRAINAGE

Catalytic, Incorporated

Prepared for:

Environmental Protection Agency

December 1971

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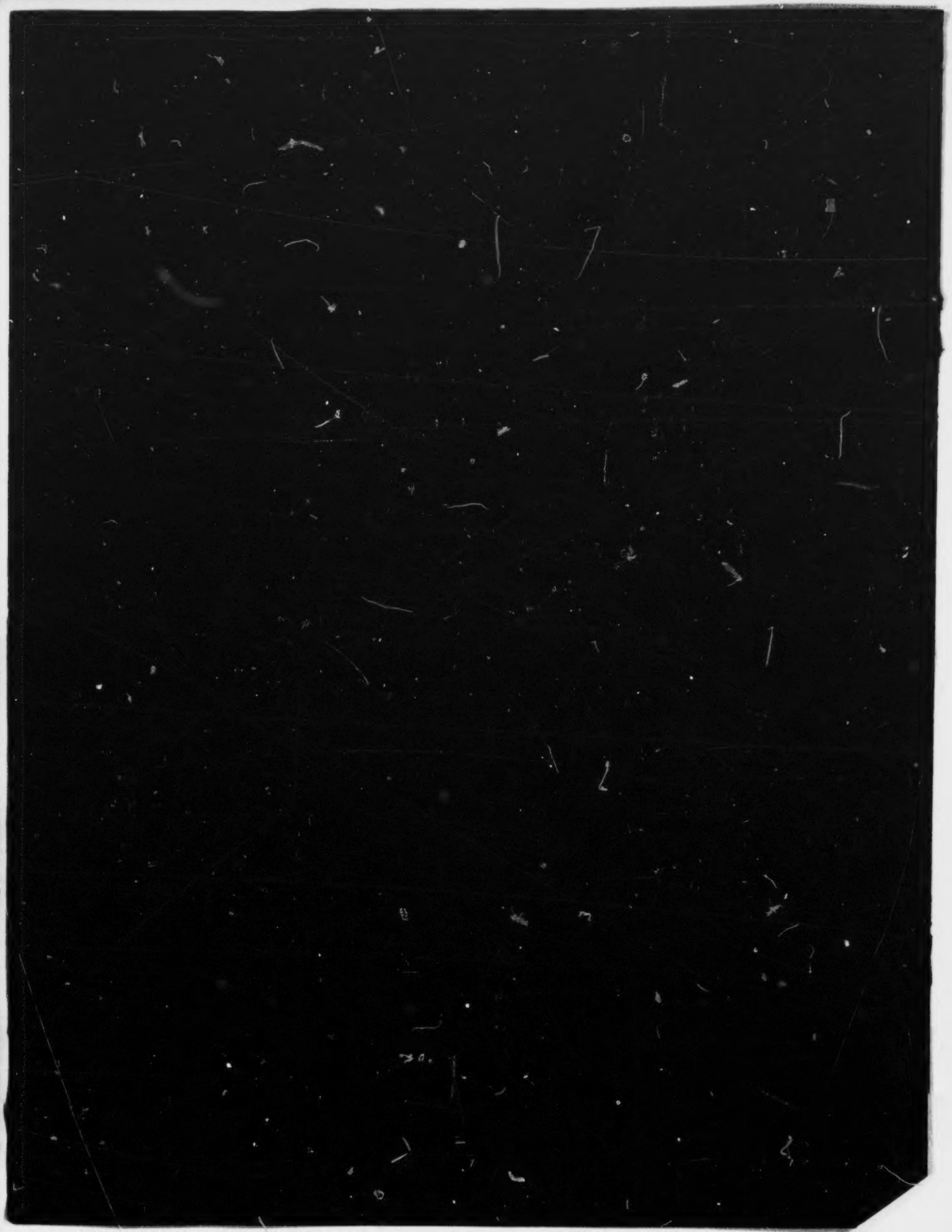

Neutradesulfating Treatment Process for Acid Mine Drainage

by

Catalytic, Incorporated
Philadelphia, Pennsylvania 19102

for the

Environmental Protection Agency

Program No. 14010 DYH
Contract No. 14-12-518

December 1971

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ABSTRACT

Acid mine drainage pollutes many of the surface streams of Appalachia. A process for the treatment and removal of the major pollutants has been developed. Iron and aluminum are removed by precipitation upon addition of controlled quantities of a neutralizer, such as sodium bicarbonate. Subsequently, a cyclic process is employed in which barium is eluted from a cation exchange resin, and reacts with the sulfate in the water to form a precipitate. Barium is continuously recovered and converted to a form which can be used to reload the partially exhausted resin. Sodium bicarbonate is also produced for use in the neutralization reaction. The only pollutant from the process, hydrogen sulfide, is converted to sulfur and is sold as a by-product. Treatment sections are included to insure complete recovery of barium from all outgoing streams. The process minimizes the cost of sludge and waste disposal while offering a product water which meets the highest interstate water quality standards. The treatment cost for a 1MM GPD Plant is $2.69 per thousand gallons of treated water. The project was terminated at the end of Phase I due to the high estimated cost of treatment.

This report was submitted in fulfillment of contract number 14-12-513 between the Federal Water Quality Administration and Catalytic, Incorporated.

Key Words: Barium elution, resins, anions, carbon dioxide pressure, ion exchange.

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(*) IR-120F is Rohm & Haas trademark for strong acid cation exchange resin of the gel type with fine -40 to +50 particle mesh and 8% cross-linked.

(**) IR-118 is a similar resin with -14 to +50 mesh particle assay (commercial grade) and 4% cross-linked.

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CONCLUSIONS

This report concerns the results of an investigation to develop a process for the treatment of acid mine drainage. The work was based on the statistical data which was developed for mine drainage samples at several sites at Norton, West Virginia and Hollywood, Pennsylvania. The process was intended for river waters containing iron and aluminum pollutants in the range of 100-1000 ppm, and sulfates in the 1000 ppm range, but is readily adaptable to waters over a wide range of compositions.

Laboratory data were presented in the report for the neutralization and precipitation of iron and aluminum using soda ash. The bicarbonate form was shown to work equally well. Variables studied include mixing and aeration time, pH, and amount of neutralizer added. Settling of the sludge was shown to be of the uniform suspension (blanket settling) type and typical curves are presented. Equilibrium data from batch testing were presented for the elution of barium from ion exchange resins in the .001 to .01 N sodium and calcium salt ranges; the selectivity ranged from 2 to 4 in favor of the calcium ion.

In the process which was developed, an ion exchange cycle is utilized to continuously remove sulfates from solution. Laboratory evidence, using a continuous bench scale apparatus, for desulfating of synthetic AMD solutions shows that for effective desulfating, the solution must contain a certain quantity of anions other than sulfate to properly elute barium from the resin and to cause precipitation of insoluble barium sulfate in the solution. A one to one ratio of anions such as chloride or bicarbonate to sulfate is needed for complete desulfating. Statistically, the acid mine drainage which has been treated to remove iron and aluminum has an insufficient amount of "other" anions in comparison to the sulfate which it contains in order to achieve maximum desulfating efficiences. Continuous laboratory desulfating runs used sulfate bearing brines in the statistical range of AMD found at the chosen sites. Near 100% sulfate removal was accomplished for solutions which had an equivalent ratio of 1:1, $Cl:SO_4$. However, for solutions with increasing amounts of sulfate over chloride ions, the desulfating efficiency decreased rapidly. By adjustments of the feed splits and the use of fresh resin feed to the first two exchangers, a 65% efficiency was attained for a 2:1 ratio solution.

Further manipulation of the system has a potential for high efficiencies even with the lower anionic concentrations of the AMD. The full development of the ion exchange model would be required to determine the practical limitations of the system.

Laboratory results show that the process would be capable of substantially reducing the concentrations of the major pollutants in acid mine waters. Virtually complete removal of iron and aluminum to a pH of 6.0 can be accomplished in the neutralization step. Use of large clarifier area along with settling tube modules in the top 2 to 4 feet of wetted wall should minimize shortcircuiting and carryover of iron--aluminum turbidity. Use

of polyelectrolyte may be necessary for charge neutralization of complexed (hydrated iron and aluminum) suspensions. Desulfating efficiencies in the exchange treatment cycle should be well above 50%, with higher ones expected with the optimization of resin-feed split adjustments. For maximum efficiencies (90-100%), a greater concentration of anions other than sulfate are needed than is present in AMD.

The process offers several advantages such as a minimum of sludge disposal problems, low operating labor cost and a light traffic schedule due to the low chemical consumption requirements. Almost all of the chemicals produced are reused in the process. The only real disposal problem is the iron-aluminum sludge from the pre-treatment-neutralization, which must be deep-welled, or further dewatered for landfill, or trucked for reclamation. The pollution effects for the process are nil, since hydrogen sulfide which is formed in the carbonation reaction is converted to by-product sulfur. Also, since barium in effluent streams is a potential contaminant, special treatment sections are designed to provide minimum barium losses. The product water should be of sufficient quality to meet the highest interstate stream standards. All of the barium sulfate which is produced will be utilized in the process for the regenerative needs of the resin.

A conceptualized design for the complete neutradesulfating process is presented in the appendix. Since it was recognized that the attractiveness of the process was due to the high purity of the water which could be produced, it was believed that a method for increasing the anionic concentration of the AMD was needed for macimum desulfating efficiencies. The method conceived was to utilize high CO_2 partial pressures in the ion exchangers under sealed conditions so that a temporary excess of ions would be present due to the bicarbonate/carbonate, carbonic acid/CO_2 equilibria. No attempt has been made to verify the method in laboratory experimentation; the equipment that was conceived necessary for this CO_2 pressurization is included as an option in the conceptualized process.

Based on the present projected or scaled up technology, the unit cost of a 1MM GPD capacity commerical unit would be $2.69/1000 gal. of feedwater based on a 30-year payback period at 4.6%. The total capital investment was estimated at $4.96 MM dollars and represents about 35% of the unit cost, or $.94/1000 gal. The contract was terminated at the end of Phase I due to the estimated high cost of treatment.

Using a six-tenths factor, the prorated unit cost for a 10 MMGPD unit would be $1.33/1000 gal., and $1.07/1000 gal. for a 25 MM GPD plant, based on 30 years at 4.6%. If the capital cost of the above units could be reduced by 50%, the costs would be $0.90/1000 gal., and $0.75/1000 gal., respectively, on the same basis. For the sized studied, increase in the size of the treatment plant does not reduce the cost of treatment significantly to make it competitive with other types of water treatment.

It is noted that fixed charges represent more than 50% of the treating cost of a 1MM GPD plant. If the high equipment cost could be substantially reduced through simplification of the process, further reductions could

be effected in the direct and indirect costs which would result in substantially reduced treating costs.

The project was terminated at the end of Phase I due to the high estimated cost of treatment.

Recommendations

The economics of the neutradesulfating system application as studied and piloted under bench scale conditions did not present a favorable projection for the statistical AMD water condition at Norton, West Virginia. The design and construction of a 15,000 GPD pilot plant for this process at this site is not recommended.

No further studies are recommended for this process on the particular statistical acid mine drainage water analysis presented for this contract based on the high estimated cost of treatment.

INTRODUCTION

Discharge from active and abandoned mines are a major source of river water pollution in the Appalachian Region of the United States. Five hundred billion gallons of mine drainage, containing 5 to 10 million tons of acid, pollute over 10,000 miles of surface streams and more than 15,000 acres of impounded waters annually (1). About 40% of the mine drainage comes from active operations and the remainder is from abandoned surface mines (25%), and shaft, drift, and auger mines (35%).

The formation of acid mine drainage stems from water of surface quality entering a mine and coming in contact with iron disulfide from rock strata and coal seams. In the presence of oxygen, ferrous sulfate and sulfuric acid form, lowering the pH; this allows other compounds containing Al, Mg, Mn, and Ca to be dissolved. Further contact with oxygen causes oxidation of ferrous to ferric sulfate and hydroxide, both of which are soluble at the low pH (2-4). In some instances, the natural ecology of the land will partially neutralize discharges within and around mine sites. Therefore, since the nature and degree of pollution will vary greatly, the best method of treatment or control will depend on the characteristics of the particular site.

Preventive measures, such as mining practices, reclamation, and control of good water supplies, can be very helpful in holding mine drainage from surface mines to a minimum. However, preventive control will not be entirely effective in every case, and for many abandoned mines, is not applicable. Source control methods are often not acceptable for active operations. In these cases, treatment of the mine drainage will be necessary to eliminate the contaminates. Therefore, to find solutions to this problem, the Federal Water Quality Administration (FWQA) of the U. S. Department of the Interior has begun a program which includes Research and Development grants to industry. These have lead to proposals for the development of methods of acid mine drainage treatment.

In April, 1969 a research contract was awarded to Catalytic, Incorporated by the FWQA to develop a process to reduce or eliminate the pollutional effects of AMD.

It was thought that a modification of a process developed by the Bureau of Mines (2) for the desulfating of seawater would have a potential to treat AMD efficiently to produce a water meeting the highest interstate stream water standards, at relatively low unit costs.

Project Breakdown

The project was divided into four phases:

Phase I - Preliminary Studies & Design
Phase II - Pilot Plant Design
Phase III - Pilot Plant Construction
Phase IV - Pilot Plant Operation (Optional)

This report deals with work conducted under Phase I of the project. The following were part of this effort:

1. A laboratory study to define design criteria for the iron and aluminum removal (pretreatment) by neutralization and the desulfating of AMD by use of cation exchange resins.

2. A development of process flowsheets for both pilot and production units.

3. Design and cost estimate of a small-scale pilot unit.

4. Development of a conceptual plant design for a neutradesulfating plant of commercial size.

5. An evaluation of the basic process feasibility.

6. An economic study to determine the cost of producing clean water at various capacity and investment levels.

7. A study to determine the marketability of $BaSO_4$ waste.(*)

Basic Process

Part of the basic process is described in "Bureau of Mines" Report RI 6928 entitled "Preliminary Process Development Studies for Desulfating Great Salt Lake Brines and Sea Water" by Darcy R. George, J. M. Riley, and Laird Crocker (2). The block diagram for this process is shown in Figure 1.

A modification of this process was the basis for Catalytic's work on a 75,000 gal./day desulfating plant to prepare sea water for feed to a desalination plant at Wrightsville Beach, North Carolina (3). The basic steps to the complete modified process are described in R&D Progress Report No. 289 entitled "Evaluation of Brine Desulfating Process as Applied to Desalination - Phase I" (4).

However, the process had to be modified for acid mine waters which are neutralized prior to desulfating, and which do not have the brine concentrations present in seawater. The new modification of the basic process includes the following steps:

1. Neutralization of AMD feed by addition of soda ash or bicarbonate to form insoluble iron and aluminum oxides and hydroxides which are removed by gravity settling.

2. Contact of the "deironized" mine drainage with the barium form of a cation exchange resin. This removes sulfate and carbonate ions as insoluble barium salts. This may include a CO_2 or flue gas pressurization.

(*) Since all $BaSO_4$ is used in the process, no such study was effected.

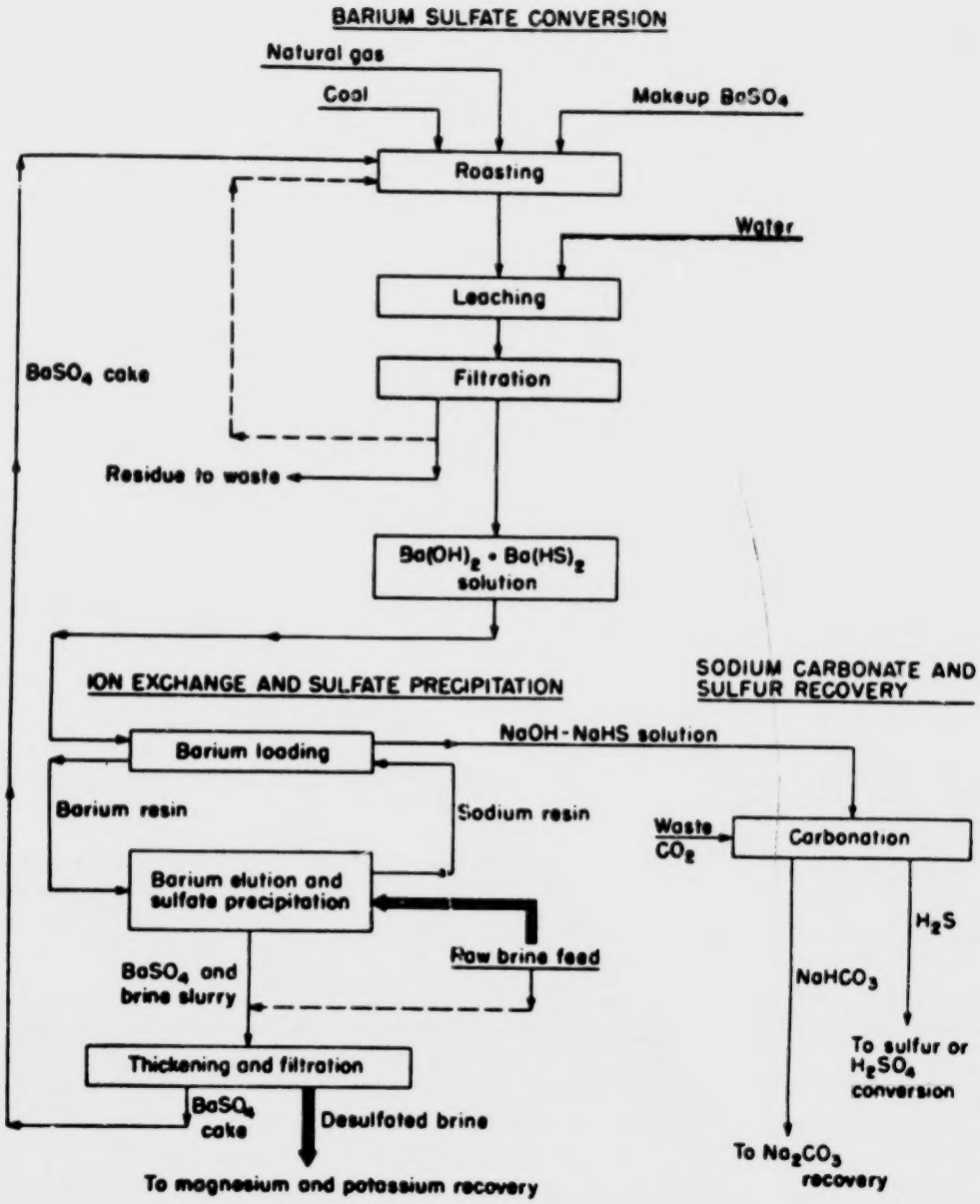

FIGURE 1. - Block Diagram for Brine Desulfating Process.

3. Separation of the desulfated, neutral mine drainage and precipitated barium salts from the resin.

4. Decarbonation and complete removal of barium from solution in the neutral, desulfated mine drainage, followed by solids separation, and final polishing of the product to eliminate carryover turbidity.

5. Conversion of calcium and magnesium forms in the partially exhausted resin to the sodium form by contact with a brine solution.

6. Conversion of precipitated barium salts to a soluble form by an atmospheric, reduction roasting with carbon (pulverized coal) mixture.

7. Leaching of the calcine to form a barium salt solution.

8. Regeneration of the partially exhausted sodium form of the resin with the barium salt solution. The effluent solution contains a sodium salt (sulfide).

9. Conversion of the sodium sulfide to bicarbonate by carbonation with CO_2 containing flue gas. Hydrogen sulfide is evolved and leaves in the flue.

10. Recovery of hydrogen sulfide by conversion to elemental sulfur.

The complete modified process block diagram is presented with the Process Description of the 1MM GPD conceptualized unit.

Steps 1, 2, 3, and 8 were carried out in bench scale operations which were conducted at the laboratories of Cyrus William Rice Co. of Pittsburgh under an FWQA authorized subcontract.

The ion exchange system had to be tested and adapted specifically for the range of dilute solutions prevalent in the AMD at the chosen sites in Norton, West Virginia, and Hollywood, Pennsylvania. This system includes the novel use of a partially exhausted resin and dilute operating ranges for the resin regeneration and carbonation sections.

An alternate pilot plant design case is also presented which would contain necessary equipment for the optional use of a pressurized ion exchange system (*), and is included as part of the conceptual design of the commercial size unit.

The overall effect of these modifications is to increase the capital investment over that which would be expected in desulfating a brine containing seawater. Contributing factors include extra equipment, greater capacities, and special materials of construction required for AMD service. There is a resultant shift in the unit cost.

(*) A pressurized unit is theoretically capable of higher desulfating efficiencies, but as yet has not been laboratory tested.

FWQA Authorization and Funding

The primary purpose of this FWQA contract is to develop an economically and technically feasible process that will reduce or eliminate the pollutional effects of acid mine waters.

The secondary purpose is to produce an effluent water that can be safely discharged into the receiving stream, which may be used by local industries or municipal water systems (5).

The Federal Water Quality Administration initiated this study with the award of a contract 14-12-518 to Catalytic on April 4, 1969.

The project was terminated at the end of Phase I due to the high estimated cost of treatment.

Ground Rules for the Study

1. The Pilot Plant shall be capable of handling 15,000 GPD of acid mine drainage. The conceptual commercial unit shall be of sufficient size to treat 1MM GPD.

2. The product water shall be of either interstate stream, potable or industrial quality.

3. A site selection and evaluation shall be made.

4. Product Water shall have a value of $0.22/1000 gal.

5. By-product values are to be taken from the current market prices.

6. The cost estimate will not include in-take facilities or sludge upgrading equipment.

7. Cost of capital is to be 4.6% for 30 years.

8. The cost of land will not be included.

9. The dollar value is to be $.0075/KWH for electricity.

The composition profile of Acid Mine Drainage which was originally suggested was not used as a basis for the design. Rather, statistical analyses were run for available stream data at Norton, West Virginia, and Hollywood, Pennsylvania sites. These are listed in Appendix A. The statistical mean for a composite of the two Norton sites was the basis for the designs presented in this report.

Preliminary Studies and Design

A 1MM GPD plant preliminary design and economic evaluation is presented in Appendix D of this report. The design of a 15,000 GPD desulfating pilot plant was also completed. The unit would include only sections which are vital in the verification of the technical feasibility of a barium loaded ion exchange resin cycle in the treatment of neutral (iron free) mine drainage feed waters. A portable (skid-mounted) design was presented which includes a description of the proposed process and equipment, flowsheets, layout plan, and material balance, along with capital cost estimates for several variations. The FWQA has made this a separate document which will be filed in their office in Washington.

EXPERIMENTAL - NEUTRADESULFATING

A laboratory study was conducted during Phase I of the contract to establish a basis of design for both the pretreatment and desulfating of acid mine drainage. Pretreatment studies were centered around treating synthetic mean Norton and Hollywood compositions with sodium carbonate. Effects of aeration and mixing time on pH were determined. Settling tests were conducted for the resulting sludge precipitates. Also tests were conducted in order to determine the efficiency of Neptune Microfloc(*) tubes in improving the settling characteristics of the sludge precipitate.

Desulfating tests were fashioned after those described by George, Riley and Crocker (2). The purpose was to determine equilibrium conditions for dilute solutions of sodium and calcium chlorides (0.1 normal and less) in batch elution runs, and to determine desulfating efficiencies of comparable solutions of sulfate bearing brines in a continuous four-stage ion exchange cycle. These tests were to study the feasibility of desulfating Norton feed water from mean down to lean Norton conditions using barium loaded resins.

Pretreatment of AMD

Theory

Iron (III) and aluminum are removed from acid mine drainage by precipitation as ferric oxide and aluminum hydroxide when the AMD is reacted with sodium carbonate or bicarbonate. There are two steps to the reaction:

Neutralization:

$$3\ Na_2CO_3 + M_2(SO_4)_3\ (**) \longrightarrow M_2(CO_3)_3 + 3\ Na_2SO_4 \qquad (I)$$

Decomposition:

$$M_2(CO_3)_3 + xH_2O \longrightarrow M_2O_3 \cdot xH_2O + 3\ CO_2$$

$$M_2(CO_3) + (3+x)\ H_2O \longrightarrow 2\ M(OH)_3 \cdot xH_2O + 3\ CO_2 \qquad (II)$$

or if bicarbonate is used (alternate):

Neutralization:

$$6\ NaHCO_3 + M_2(SO_4)_3 \longrightarrow 2M(HCO_3)_3 + 3\ Na_2(SO_4) \qquad (IA)$$

(*) Mention of commercial products does not imply endorsement by the Federal Water Quality Administration.

(**) M = Mineral

Decomposition:

$$2\ M(HCO_3)_3 \longrightarrow 2\ M(OH)_3 + 6\ CO_2 \qquad \text{(IIA)}$$

The CO_2 that is formed during the decomposition step will react with the available carbonate and the following reversible reaction occurs:

$$Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3 \qquad \text{(III)}$$

The equilibrium ratio of bicarbonate to carbonate is a function of the CO_2 partial pressure, sodium normality, the solubility of CO_2, and the temperature. The final pH of the solution depends on this ratio.

If some of the iron is in the ferrous form it must be sparged with air so that insoluble ferric hydroxide will be formed. The oxidation reaction is as follows:

$$4\ Fe(OH)_2 + 6H_2O + O_2 \longrightarrow 4\ Fe(OH)_3 + 4H_2O \qquad \text{(IV)}$$

This indicates that one pound of air is needed to oxidize 2.5 lbs of ferrous hydroxide; however, a large excess of air is required to bring about a reasonable rate.

Composition of the Feedwater

Statistical analyses were conducted to determine the range of ionic concentrations which would be present in AMD at the Hollywood, Pennsylvania, and Norton, West Virginia sites. These may be found in Appendix A (Tables V to XIV).

Since most of the iron is in the ferric form at the Norton site, aeration to oxidize ferrous to ferric iron is of secondary importance. However, at the Hollywood site, aeration time and rate are critical since the ferrous form predominates.

Pretreatment Tests

For most of the tests which were conducted, synthetic acid mine drainage solutions were composed of iron solutions in the 1000 ppm and 100 ppm range to resemble what was thought to be mean Hollywood and Norton feedwater compositions, respectively. However, statistical data later received from the Hollywood site in general, were much lower in iron concentration than was originally anticipated; Proctor Number 2 had a mean iron (II) concentration of 850 ppm, and Proctor Number 1 had 250, but all the others had iron concentrations below 100 ppm; thus, the average value of the combined streams is expected to be closer to the Norton mean of 120 ppm iron (III).

The tests were run by adding a measured amount of soda ash solution to a 500 cc synthetic solution consisting of dissolved iron, aluminum, and calcium sulfates, with sulfuric acid added in some cases to dissolve the salts.

Subsequently, the treated solutions were mixed for 1-2 hours, air sparged for 1/2 hour, and then introduced to a 500 cc graduated cylinder in which quiet settling was observed for 2 hours.

Appendix B, Table XV is a summary of the pretreatment tests, and Table XVI shows the settling rates of the corresponding sludges. These results show that the addition of near stoichiometric amounts of soda ash result in an immediate rise of pH to between 5 and 6. Thus, reactions I and II are instantaneous. However, the reactions rates for III and IV are much slower, and, in general, require an hour for mixing and air sparging.

Some of the results are plotted in Appendix B. Figure 6 shows aluminum and iron (III) residual concentrations as a function of pH; and Figure 7 gives the bicarbonate concentration and pH as a function of the amount of soda ash added. Figure 8 is a typical curve for treatment of iron rich solutions with soda ash. From Figure 7, it is noticed that less than a stoichiometric quantity of soda ash (90-96%) is required for complete iron and aluminum removal. This is due to precipitation of some unreacted iron and aluminum sulfates at pH of 5 to 6. However, the iron concentration of Figure 6 increased rapidly as the pH decreases below 6; therefore, pH is the limiting and controlling factor in soda ash addition.

The sludge resulting from soda ash pretreatment of synthetic acid mine drainage solutions consists of hydrated iron and aluminum oxides and hydroxides, along with some calcium carbonates.

Tests were also run using the bicarbonate rather than soda ash; they show only slight differences in the pretreatment curve and the same overall effect will be realized.

The two-hour settling tests were run in a 500 cc graduated cylinder. In the Appendix B, Figures 10 and 11 show the sludge volume measured at the interface (cc.) as a function of time. The iron rich solution (1150 ppm) experienced strong spherical interferences resulting in the hindered settling characteristics; the "lean" iron curve containing 120 ppm as in the mean Norton feedstream, was much steeper, thus requiring a smaller thickener area. Table I below shows the final dilution ranges of typical AMD solutions.

TABLE I

Volume Occupied by Pretreated AMD Sludges

Iron (III)	V%(*)	W% Solids
1150 ppm	20-35%	0.8-1.3%
120 ppm	4-7%	0.8-1.1%

(*) Based on final dilution volume.

The conclusions drawn from the pretreatment testing were used to establish the following criteria for the process design.

1. Soda ash should be added in line to allow a solution of approximately 6.0 pH to enter the reactor.

2. One hour retention time with vigorous agitation and simultaneous pressurized air sparging in a back-mix reactor will be sufficient to oxidize ferrous iron, remove any excess CO_2, precipitate remaining iron and aluminum, and sustain a bicarbonate/carbonate residual environment which is favorable for the desulfating process.

3. A requirement of 2400 square feet per ton dry solids per day along with 8 feet wetted wall, would provide for sufficient sludge thickening.

It is believed that net point charges on individual particles may generate an electric field which would bring about the formation of colloids, thus preventing agglomeration of the spheres due to these interferences. As the concentration increases these interferences offer a greater hindrance to particle settling. Use of a dispersant, or a flocculent, could result in formation of large groups of neutral clusters which rapidly settle. Further investigations are warranted, using a variety of industrial polyelectrolytes.

Desulfating of AMD

Introduction

Sulfate is removed from neutralized (pretreated) acid mine drainage when the AMD is contacted with a strong acid cation exchange resin which is loaded with barium. The rate of desulfating is a function of the rate at which barium can be eluted from the resin. Studies were conducted to determine elution rates and desulfating efficiencies and the factors which affect the same. These tests were of two types:

1. Batch Elution Tests were run to determine equilibrium conditions for synthetic solutions of sodium and calcium salts in the 0.001 to 0.1 normal range.

2. Continuous desulfating runs were conducted to determine the factors involved in offsetting and preventing the attainment of equilibrium, and the degree to which it could be accomplished. By the use of these factors, a temporary environment of barium ions over the equilibrium concentration could be maintained in solution to bring about complete sulfate removal.

Model

During the course of these tests, the following reaction model was developed which served as a basis and guide for the study (6). When a particle of barium loaded resin is placed in contact with an ionic solution bearing sulfates, the following steps occur:

1. Diffusion of cation (other than barium) to the site (resin surface).

2. Diffusion of same from the surface into the porous resin.

3. Displacement (Elution) of barium by the cation according to the reactions:

$$2M^{+} + BaR_2 \rightleftharpoons 2MR + Ba^{++} \qquad (V)$$

$$M^{++} + BaR_2 \rightleftharpoons MR_2 + Ba^{++}$$

(NOTE: M = Alkali or Alkaline Earth Metal Ion)

4. Barium diffusion through the pore solution to surface of resin or desorption.

5. Barium diffusing into the bulk solution.

6. Barium reaction with sulfate ions:

$$Ba^{++} + SO_4^{=} \longrightarrow BaSO_4 \qquad (VI)$$

7. Barium sulfate precipitation (crystallization)

8. Barium sulfate crystal growth

The first five steps are reversible by nature and require the existence of comparable anions that will yield a soluble barium salt (e.g.: HCO_3^- or Cl^-). If only sulfate anions were present in quantity, then steps 4 and 5 would not occur and barium sulfate would form and precipitate in the resin pores, thus resulting in "blinding" of the resin. This blinding effect coupled with the relative immobility of the "bulky" sulfate ions results in very low desulfating efficiencies. Steps 1 to 5 can be lumped as the equilibrium section, whereas steps 6, 7, and 8 are thermodynamically favorable and irreversible and are the non-equilibrium part. The former is the slower and therefore rate controlling part of this heterogenious system.

To insure that the formation of the solid barium sulfate product does not terminate or inhibit its own propagation, the equivalents of dissolved barium in the bulk solution must be greater than or equal to the sulfate. Thus, desulfating efficiency would be high for feed solutions containing an anion(*)/sulfate ratio of one or more. However, the percent of desulfating would decrease rapidly as the ratio dropped below 1.

Development of a Pressurized Desulfating System

Since the Norton feedwater profile in Table II indicates that the sulfate in the "mean" water is about 0.019 normal, over 1100 ppm bicarbonate would be required for a ratio of 1. However, only 100 ppm is expected to be present in mean Norton pretreated feedwater.

One solution is to add an additional quantity of sodium bicarbonate or carbonate to the desulfating section feed stream. However, this would be costly due to high sulfuric acid requirements for decarbonation. A more economical approach is to use pressurization with CO_2 and create a "temporary" 1:1 ratio in the barium exchanger train due to formation of bicarbonate under high CO_2 partial pressures. The reaction

$$Na^+ + H_2CO_3 \rightleftharpoons NaHCO_3 + H^+ \qquad \text{(VII)}$$

would therefore be thermodynamically favorable under such conditions. The initial pressures would be high (75 psig) due to high initial sulfate concentration, and would be gradually reduced until only about 3 psig remains in the last exchanger due to previous partial desulfating.

One last possibility is to maintain CO_2 pressures from the pretreatment sections, but this is thought to greatly hinder iron removal due to reaction of the hydroxide with CO_2 to form iron bicarbonate which could be favorable under high CO_2 partial pressures.

Further experimentation either in bench or pilot scale is needed to verify the pressurized desulfating model.

Factors Influencing Barium Elution

Providing sufficient contact time between the resin and solution for the replacing cations to diffuse into the resin and to desorb barium is the first requirement of the ion exchange desulfating. However, enough barium must be in solution to cause the solid to form mainly in the bulk solution and not in the resin. This is accomplished by always maintaining conditions which are favorable for the barium elution reaction (V) to shift toward the right. Thus, non-equilibrium conditions must be maintained. This environment is created in two ways:

(*) Other than sulfate

TABLE II

NORTON FEED WATER PROFILE (*)
FROM STATISTICAL TABULATIONS

Item	MINIMUM		MEAN		MAXIMUM	
	PPM	N x 10^3	PPM	N x 10^3	PPM	N x 10^3
Iron (III)	26	2.60	113	10.0	229	20.3
Aluminum	11	1.20	35	3.4	72	8.0
Calcium	37	1.85	104	5.2	152	7.6
Magnesium	14	1.15	37	3.0	88	7.2
Sulfate	270	5.60	904	18.8	1650	34.4

(*) A combination of Grassy run and a side tributary.

1. Split the resin feed among the exchangers so that freshly loaded resin is being constantly introduced over the entire system. This will increase the amount of barium eluted throughout since a high fraction of barium on the resin is maintained over the entire system.

2. Introduce feed solution to all the exchangers at a pre-set ratio. This monitors the ratio of "other" anion/sulfate in order to perpetuate the barium sulfate reaction (VI) in solution throughout the system. Therefore, equilibrium between the barium on the resin and barium in solution is never attained due to the constant need for the latter because of a continuous introduction of sulfate bearing solution.

Elution Rate Studies

The rate of elution of barium from Amberlite(*) IR-120, 14 to 50 mesh, 120F, 40 to 50 mesh, both 8% cross-linked, and IR-118, 14 to 50 mesh particle assay, 4% cross-linked resin was studied in small scale tests using brine solutions of varying normality. The purpose was to study the various parameters of the equilibrium part of the model and to determine the degree of elution with normalities as low as 0.003N Na^{+}, and 0.002N Ca^{+2}, which are approximately the conditions of lean Norton feedwater (see Table II). The tests were conducted by vigorously mixing 42 ml. of wet settled barium loaded resin with one liter of solution for 20 minutes. The slurry was separated by filtration; then the same resin was mixed with a fresh portion of solution for the same period as before. The test period was generally 120 minutes (6 cycles).

After initial problems due to improper resin loadings were overcome, the following were affirmed as is evidenced in Table III:

1. The resin is highly selective toward calcium over sodium; the selectivity range is 2.0 - 3.9(**); this increases with the elution time and the decrease of barium on the resin.

2. There is a slight advantage of the higher available exchange area of the more open 4% cross-linked resin over the 8% cross-linked. The specific loading of the coarse, open resin was measured as 180-185 gram barium per liter of wet barium loaded resin compared to 215-225 for the fine, 8% resin.

3. Earlier tests which were run during adverse loading conditions indicated that the fine particle assay resin (40 to 50 mesh) had a slight advantage over the coarse (14 to 50 mesh) resin.

(*) Rohm & Haas Co. trademarks for strong acid cation exchange resins. Mention of commercial products does not imply endorsement by the FWQA.

(**) Sodium taken as the base value (1.0).

TABLE III

BATCH ELUTION OF BARIUM BY BRINE SOLUTIONS

SOLUTION	RESIN TYPE	PERCENT BARIUM ELUTED	
		One Cycle	Six Cycles
0.1N $CaCl_2$	IR-118	27	72
0.1N $CaCl_2$	IR-120 F	22	58
0.1N NaCl	IR-118	10	25
0.1N NaCl	IR-120 F	8	23
0.05N $CaCl_2$	IR-118	18	58
0.05N $CaCl_2$	IR-120 F	15	47
0.05N NaCl	IR-118	6	16
0.05N NaCl	IR-120 F	5	13
0.02N $CaCl_2$	IR-118	11	41
0.02N $CaCl_2$	IR-120 F	9	33
0.02N NaCl	IR-118	3.2	8.6
0.02N NaCl	IR-120 F	2.7	7.2
0.01N $CaCl_2$	IR-118	7.3	27.4
0.01N NaCl	IR-120 F	2.0	5.8
0.005N $CaCl_2$	IR-118	4.2	19
0.005N $CaCl_2$	IR-120 F	3.3	15.5
0.005N NaCl	IR-118	1.4	4.6
0.005N NaCl	IR-120 F	1.1	3.3
0.002N $CaCl_2$	IR-118	2.6	10.4
0.002N $CaCl_2$	IR-120 F	1.8	7.8

Figures 12 to 15 in Appendix C contain more detailed information on the elution of barium from sodium and calcium chlorides using IR-120F and IR-118. In these figures, the fractions of the initial barium concentration remaining in the resin are shown as a function of the number of cycles (20 minutes per cycle).

These results can be applied to a system in which a sulfate bearing brine is used. A 0.02N NaCl solution could elute less than 9% of the barium in 120 minutes, and 0.005N NaCl could elute only half that amount. If a 0.005 sulfate normality were present with the 0.005N chlorides (1:1 ratio), enough barium would be eluted from the resin in 120 minutes for complete desulfation. This, however, is assuming that a large excess of resin is used, with fresh feed solution to six separate equilibrium stages (cycles). However, for a 0.02N NaCl solution, only about 0.01N barium could be eluted in 120 minutes, which would result in only 50% desulfating in the above systems. Therefore, it was thought that in addition to large excesses of resin, it would be necessary to introduce fresh resin feed at certain stages of the cycle. Using the same theoretical equilibrium model, fresh resin feed to the first five stages would be sufficient for 100% desulfating for a 0.02N sulfate solution. However, as the chloride/sulfate ratio decreases below 1, complete desulfation becomes impossible in the range under consideration. This range coincides with the mean and lean Norton normalities.

Also included in Appendix C are Figures 17 to 20 which demonstrate the absolute amounts of barium eluted in each successive equilibrium stage. The slope of these curves between successive stages (cycles) gives an indication of the relative feed solution splits which would be used in a continuous operation having a staged cascaded ion exchange arrangement with split stream feeds. However, due to use of split resin feeds and varying sulfate concentrations in the actual system, the optimum proportion must be determined experimentally.

Figure 21, Appendix C, shows the effect of using bicarbonate in place of chloride anions in the elution of barium. The use of bicarbonate ions therefore appears to be comparable, though slightly less favorable due to decreased mobility.

Figures 2 to 5 show the equilibrium curves for these runs. They exhibit the increase in favorable conditions with increasing normality, and with calcium over sodium ions. The upper dotted line represents the fully loaded barium resin. It is noted that as the concentrations decrease, the curves become more hyperbolic. This allows a clearly defined cut point to be determined. At this point, the maximum economical theoretical stages is established. Beyond this point, each

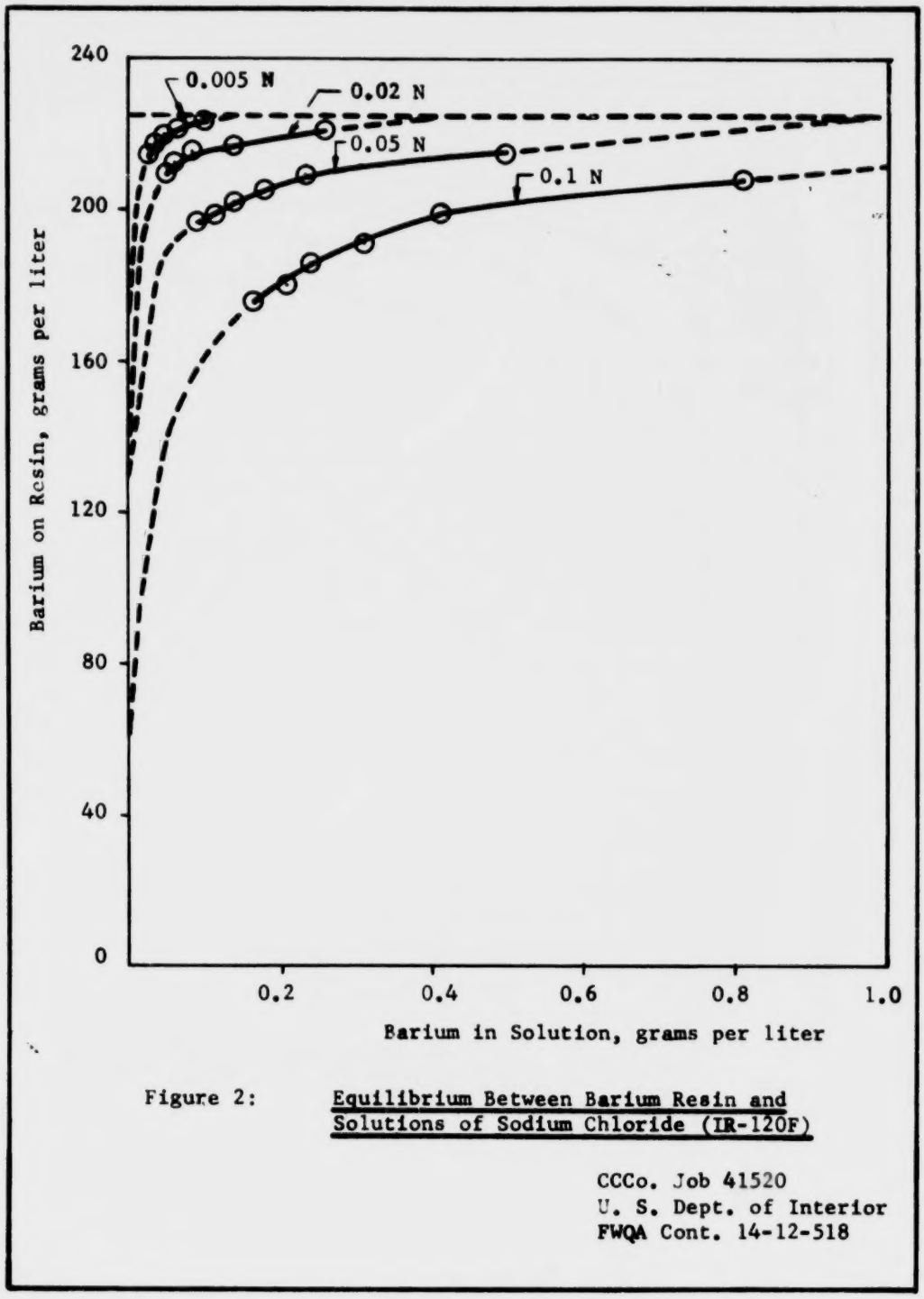

Figure 2: Equilibrium Between Barium Resin and Solutions of Sodium Chloride (IR-120F)

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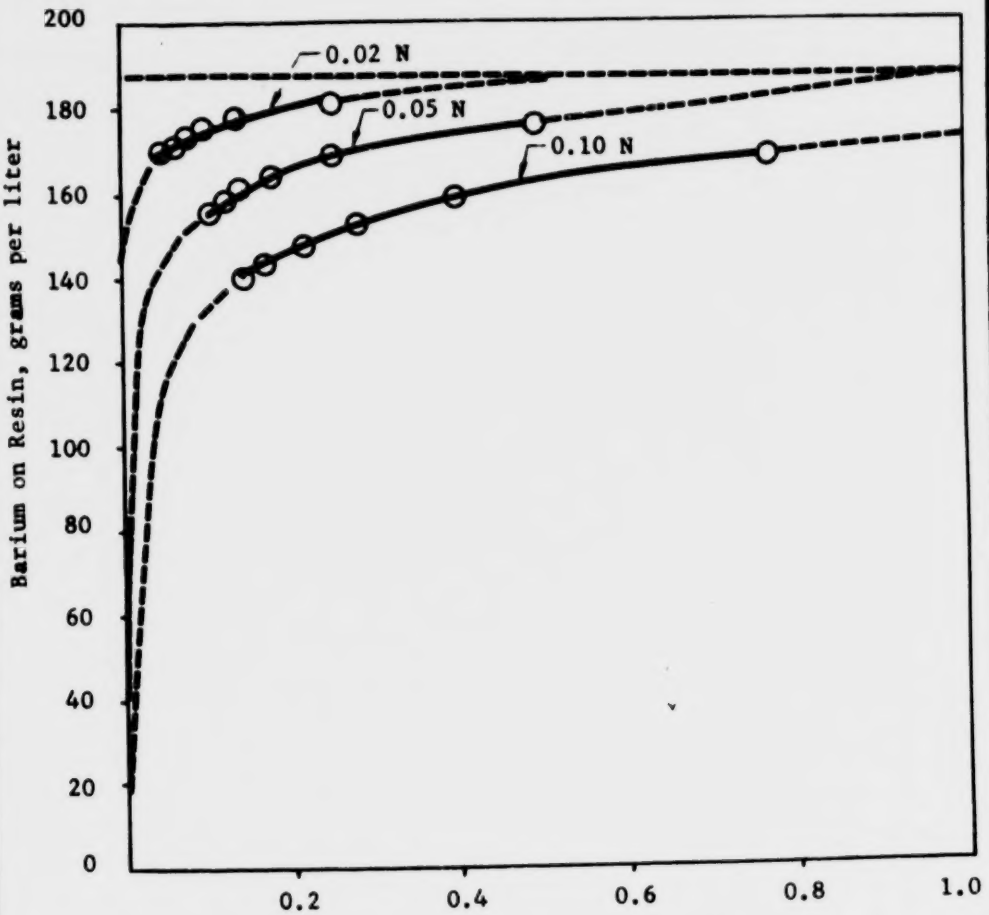

Figure 3: Equilibrium Between Barium Resin and Solutions of Sodium Chloride (IR-118)

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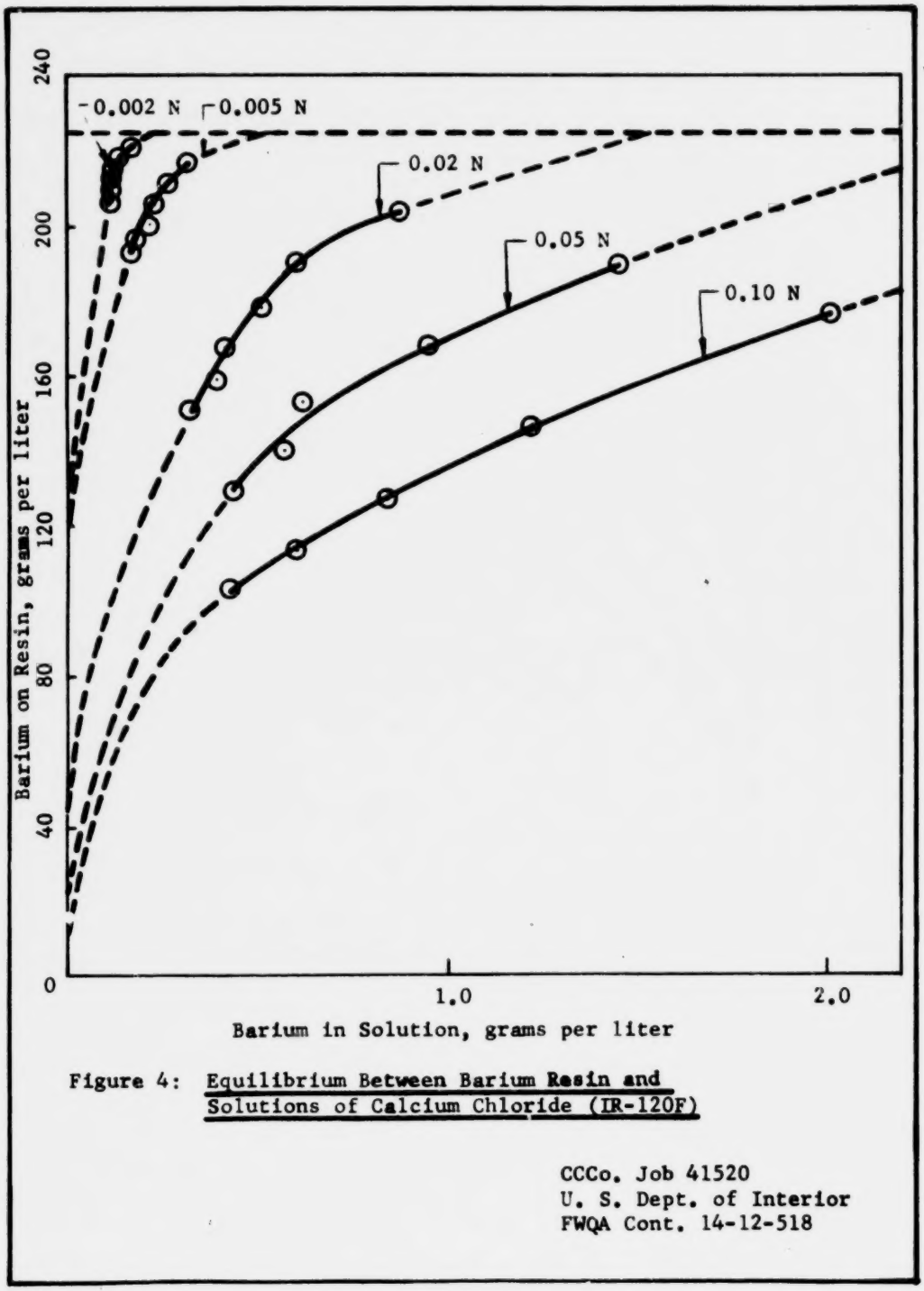

Figure 4: Equilibrium Between Barium Resin and Solutions of Calcium Chloride (IR-120F)

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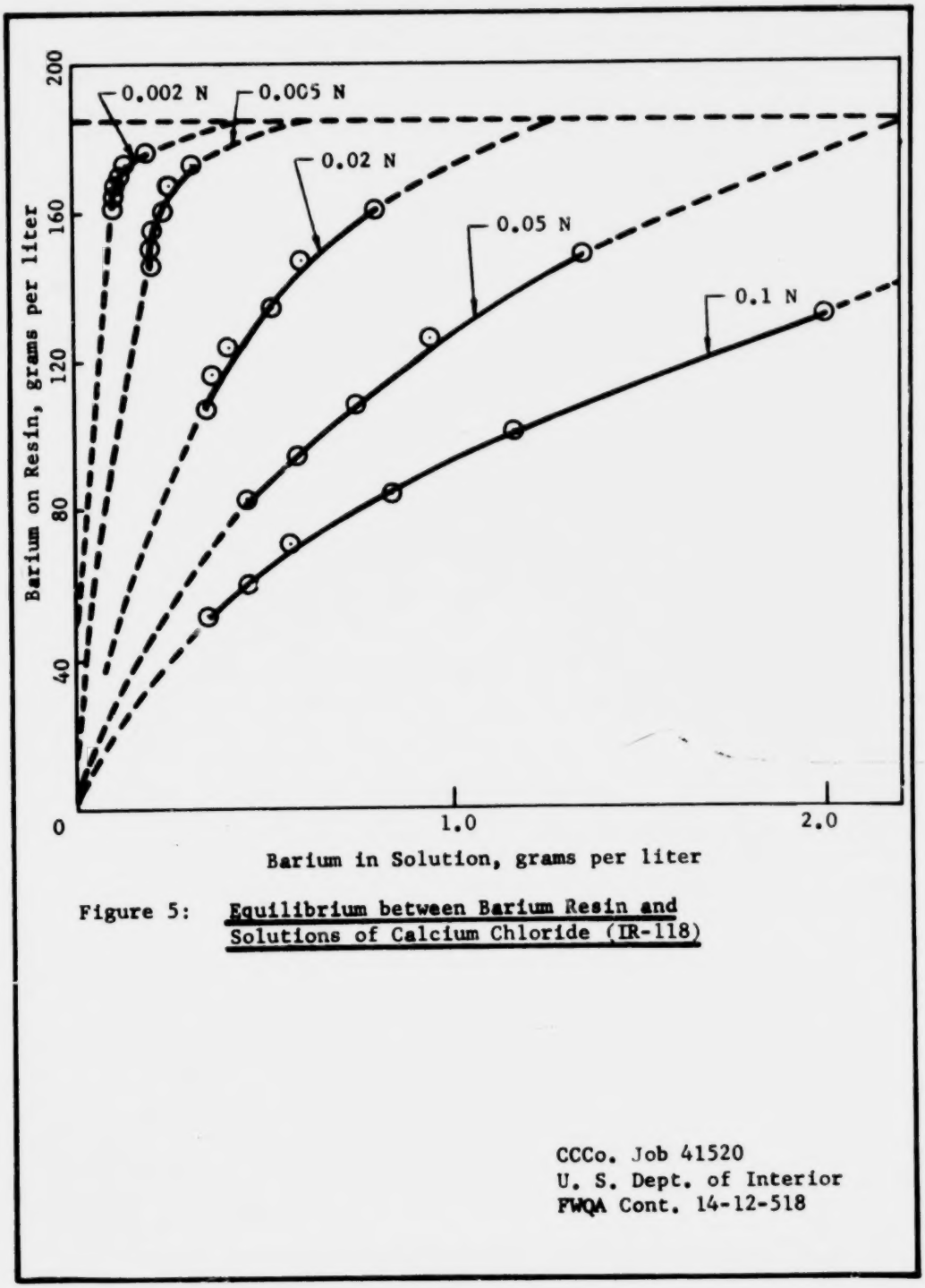

Figure 5: Equilibrium between Barium Resin and Solutions of Calcium Chloride (IR-118)

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successive equilibrium stage results in only a small additional amount of barium in solution. Thus, an increasingly large number of stages is required to bring about relatively small increases in desulfating efficiency. These curves again illustrate the desirability of using a small number of stages with a large excess of resin in each stage.

Continuous Tests

In the continuous tests, the desulfating of feeds consisting of sulfate bearing brines was attempted. Thus, the complete desulfating model was studied together.

The apparatus used resembles the one described in the Bureau of Mines Report (2). It is shown in Figure 16, Appendix C. The main difference is in the addition of the split resin feed. The variables studied were resin type, normality of the mother liquor, resin and feed splits, and the molar ratios of both $Ba:SO_4$ and $Cl:SO_4$.

In the operation, a loaded, washed resin was continuously fed by a peristaltic pump to the first bucket(*) at 2 to 4cc/min. The synthetic sulfate bearing brines were continuously metered to each of the tanks through individual rotameters at a combined rate of 170 cc/min. to provide an overall residence time of 110 to 120 minutes. The plastic tanks were equipped with variable speed agitators and were covered to avoid resin loss due to splashing.

At startup, the first tank was partially filled with a small amount (1000 cc) of a dilute sodium or calcium chloride solution which was usually of the same normality as in the feed solution so as not to mask the results. A small amount (6 to 24 cc) of barium loaded resin was then mixed for 20 minutes with this solution in order to initiate the reaction. Thus, by eluting barium from the resin, an initial concentration of barium in the feed solution was assured.

The feed solution flow was then started to the first tank. After the overflow from the first tank filled the second, the brine feed to the second was turned on, and so on down the line. Samples were taken from each exchanger at one hour intervals from the time of overflow of that tank. The samples were tested for pH and sulfate. The resin feed rate was measured regularly, but was found to vary greatly during short periods of time due to the cyclic pump characteristics, and the average values were used. However, the solution feed rates were kept constant.

(*) A second pump was later installed in order to feed resin to exchangers 2 and 3.

Table IV is divided into two parts; the "A" section summarizes those runs in which the ratio of the sulfate to chloride normality is 1. The "B" section is composed of those runs in which the ratio is greater than 1. In general, the table shows that equilibrium conditions are favorable for those solutions which are of type "A." Furthermore, 4 x the stoichiometric amount of resin was a definite improvement over 2 x the amount, for the runs in which the -40 to +50 mesh 8% cross-linked resin was used. In "A" type runs where calcium salt was used, a $Ba:SO_4$ ratio of 2 was sufficient; however, when sodium ion was used in place of some of the calcium, a ratio of 4 was required for 100% desulfating.

For the cases where the ratio of SO_4:Cl was greater than 1, designated as "B" solutions, the desulfating percent dropped notably as the ratio was increased. The use of a higher resin rate did not have the significant effect that was noticed for the type "A" solutions; however, splitting the resin feed to two tanks improved the efficiency threefold when the feed solution splits were also adjusted. It was believed at this time that proper adjustment of this split in combination with a resin feed to three tanks, using a high ratio $Ba:SO_4$ could result in high desulfating efficiencies for solutions in which the SO_4:Cl ratio was not so favorable. This could significantly reduce the need for pressurization or bicarbonate addition. Further experimentation would be needed to verify these theories, in either pilot or bench scale operations.

Filtration

A settling test, using Neptune microfloc inclined tubes instead of a clarifier reaction zone, indicated that the settling properties of neutralized AMD would be improved. A 2.5 liter synthetic Norton type solution of 117 ppm Fe^{+3}, 35 ppm Al^{+3}, and 100 ppm Ca^{+2}, and an iron rich solution of 1000 ppm Fe^{+3} were both neutralized by soda ash. A 3-inch by 3-inch square tube proved to be adequate for the lean solution and a five fold increase in settling rate over "quiet" settling was the result. However, the iron rich sludge filled the vertical section at a pumping rate of 50 ml/min. This was due to inherent limitations of the "as built test unit," and the run was cancelled. However, at a relatively small additional cost in comparison to that of the clarifier, the tubes could be installed in the reaction zone of a conventional clarifier, and this would insure a high clarity overflow liquor.

TABLE IV

CONTINUOUS ION EXCHANGE DESULFATING RUNS

A: Solutions with $SO_4^{=}/Cl^{-}$ = 1.0

TEST	819	822	826	829	912	918	919	922	926
Solution Normality,									
Sodium Sulfate	0.01	0.01	0.01	0.01	0.005	0.005	0.01	0.01	0.01
Sodium Chloride	-	-	-	0.01	-	-	0.005	0.008	0.008
Calcium Chloride	0.01	0.01	0.01	-	0.005	0.005	0.005	0.002	0.002
Total Solution Feed, cc/min.	170	170	170	170	170	170	170	170	170
Stage 1	90	90	90	90	90	90	90	90	90
Stage 2	50	50	50	50	50	50	50	50	50
Stage 3	20	20	20	20	20	20	20	20	20
Stage 4	10	10	10	10	10	10	10	10	10
Resin Type	IR-120F	IR-120F	IR-120F	IR-120F	IR-118F	IR-120C(*)	IR-120F	IR-120F	IR-120F
Loading, gm/liter	225	225	225	225	181	237	228	228	228
Total Resin Feed, cc/min.	2	4	2	2	2	2	2	2	4
Stage 1	2	4	2	2	2	2	2	2	4
Stage 2	-	-	-	-	-	-	-	-	-
Equivalents - BA:SO_4	3.86	7.73	3.86	3.86	6.22	8.03	3.90	3.90	7.80
Equivalents - SO_4:Cl	1	1	1	1	1	1	1	1	1
Run Duration, min.	240	210	395	200	350	360	240	240	350
Sulfate Concentration, ppm									
Stage 1	99.5	93.5	97.9	100.0	96.9	98.4	99.4	63.3	100
Stage 2	99.5	92.3	88.0	86.6	100.0	98.4	99.4	50.0	100
Stage 3	72.2	93.8	76.4	81.5	100.0	99.0	99.4	47.9	100
Stage 4	92.1	93.5	68.4	85.6	100.0	99.0	99.4	43.8	100
Initiant - 1000cc									
Normality, $CaCl_2$	0.05	0.05	0.05	0.10(**)	0.01	0.01	0.01	0.01	0.01
Resin, cc	18	18	18	18	11.8	11.8	11.8	11.8	24.0

(*) Rohm & Haas Co. trademark for strong acid cation exchange resin of the gel type with -14 to +50 mesh particle assay (commercial grade) and 8% cross-linked.

(**) NaCl

TABLE IV

CONTINUOUS ION EXCHANGE DESULFATING RUNS

B: Solutions with $SO_4^{=}/Cl^{-} > 1.0$

TEST	814	820	903	908	909	924	930	1001	1006
Solution Normality									
Sodium Sulfate	0.01	0.01	0.03	0.01	0.005	0.01	0.01	0.01	0.01
Sodium Chloride	-	-	-	-	-	-	-	-	-
Calcium Chloride	0.005	0.005	0.002	0.002	0.002	0.005	0.005	0.005	0.005
Total Solution Feed, cc/min.	170	170	170	170	170	170	170	170	170
Stage 1	90	90	90	90	90	40	40	90	70
Stage 2	50	50	50	50	50	70	70	50	70
Stage 3	20	20	20	20	20	40	40	20	20
Stage 4	10	10	10	10	10	20	20	10	10
Resin Type	IR-118	IR-118	IR-120F	IR-120F	IR-120F	IR-118	IR-120F	IR-120F	IR-120F
Loading, gm/liter	187	181	225	225	228	187	228	228	228
Total Resin Feed, cc/min.	2	4	6	2	1	4	4	4	4
Stage 1	2	4	6	2	1	4	2	2	2
Stage 2	-	-	-	-	-	-	2	2	2
Equivalents - BA:SO_4	3.08	15.2	3.86	3.86	3.88	6.40	3.9/7+(*)	3.9/7+(*)	3.9/7+(*)
Equivalents - SO_4:Cl	2	2	15	5	2.5	2	2	2	2
Run Duration, min.	110	276	335	325	335	240	225	345	240
Sulfate Concentration, ppm									
Stage 1	24.3	23.0	8.76	20.1	32.9	100.0	99.4	19.8	37.5
Stage 2	12.8	17.2	-	-	15.7	48.0	100	19.8	33.3
Stage 3	17.9	14.8	-	-	28.6	26.5	67.8	20.8	35.4
Stage 4	21.4	17.2	5.88	12.3	41.0	26.0	64.6	19.8	29.2
Initiant - 1000cc									
Normality, $CaCl_2$	0.01	0.05	0.03	0.01	0.005	0.01	0.01	0.01	0.005
Resin, cc	11.7	18	35.4	11.8	5.9	23.6	24.0	24.0	24.0

(*) To Stage 1; Additional Resin added to Stage 2 @ 3.9 BA:SO_4 to bring total to over 7.

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* * * *

The objective of this project was to investigate a potentially low cost treatment method for mine drainage pollution control. Although the results of this investigation indicated the treatment method could possibly be successful, the high cost of purified water as indicated by the first Phast study dictated that the method not be investigated further. This project of EPA was conducted under the direction of the Pollution Control Analysis Section, Ernst P. Hall, Chief, Donald J. O'Bryan, Jr., Program Manager, and Robert B. Scott, Project Officer.

List of manufacturers contributing to the equipment cost estimate:

Name	City, State
Worthington Corporation	Philadelphia, Pa.
Neptune Meter Co.	Philadelphia, Pa.
Graver Water Conditioning Co.	Philadelphia, Pa.
Sweco, Inc.	Philadelphia, Pa.
Eastern Industries	Philadelphia, Pa.
Vanton Pump & Equipment Corp.	Philadelphia, Pa.
Dorr-Oliver, Inc.	Philadelphia, Pa.
Pennwalt Corp.	Philadelphia, Pa.
Cleveland Mixer Co.	Philadelphia, Pa.
Mixing Equipment Co., Inc.	Philadelphia, Pa.
AMF Cuno Division	Philadelphia, Pa.
FMC, Corp.	Homer City, Pa.
Mitchell Plastics, Inc.	Pittsburgh, Pa.
Agile Division: Walge Co.	Philadelphia, Pa.
International Salt Co.	Clarks Summitt, Pa.
Penna. Pump & Compressor Co.	Easton, Pa.
Bartlett-Snow Division	Philadelphia, Pa.
Rex Chainbelt, Inc.	Philadelphia, Pa.
Pulverizing Machinery Division	Philadelphia, Pa.
Meyer Machine Co.	San Antonio, Texas
Rohm & Haas Co.	Philadelphia, Pa.
Croll-Reynolds Engineering Co., Inc.	Stanford, Conn.

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APPENDIX A

STATISTICAL ANALYSIS

OF

AMD

TABLE V

STATISTICAL ANALYSIS OF AMD

Norton Site - Composite

No.	Item	Mean	Standard Deviation	Population	Minimum	Maximum
1.	Flow CFS	6.64	6.25	91	0.80	23.0
	GPM	2,980.	2,800.	-	359.	10,300.
	MMGPD	4.29	4.04	-	0.52	14.9
2.	pH	2.77	0.17	82	2.50	3.30
3.	ACIDITY as ppm $CaCO_3$	609.	180.	82	83.1	947.
4.	Fe total, ppm	113.	39.7	82	26.0	229.
5.	Fe^{+2}, ppm	4.13	1.42	22	2.00	7.20
6.	SO_4^{-2}, ppm	904.	263.	82	270.	1,650.
7.	HARDNESS as ppm $CaCO_3$	411.	120.	82	151.	744.
8.	Ca^{+2}, as ppm $CaCO_3$	259.	72.3	40	92.0	380.
9.	Ca^{+2}/HARDNESS	0.68	0.54	40	0.59	0.86
10.	Mg^{+2}, as ppm $CaCO_3$	152.	47.6	-	59.0	364.
11.	Al^{+3}, ppm	35.3	10.7	40	11.0	72.0
12.	CONDUCTIVITY, Micro-mhos @ 25°C	1,570.00	427.	82	150.	2,250.

TABLE VI

STATISTICAL ANALYSIS OF AMD

Norton Site - Stream G-1A

No.	Item	Mean	Standard Deviation	Population	Minimum	Maximum
1.	Flow CFS	7.94	15.2	26	0.80	80.
	GPM	3,560.	6,800.	-	359.	35,900.
	MMGPD	5.13	9.80	-	0.52	51.7
2.	pH	2.77	0.13	26	2.60	3.10
3.	ACIDITY as ppm $CaCO_3$	525.5	216.	26	83.1	947.
4.	Fe total, ppm	115.	44.7	26	26.0	210.
5.	Fe^{+2}, ppm	-	-	-	-	-
6.	SO_4^{-2}, ppm	717.	211.	26	270.	1,120.
7.	HARDNESS as ppm $CaCO_3$	340.	98.20	26	151.	492.
8.	Ca^{+2}, as ppm $CaCO_3$	231.	69.30	26	92.0	330.
9.	Ca^{+2}/HARDNESS	0.70	0.10	26	0.60	0.90
10.	Mg^{+2}, as ppm $CaCO_3$	109.	28.9	#7 - #8	59.0	162.
11.	Al^{+3}, ppm	31.0	9.10	26	11.0	45.
12.	CONDUCTIVITY, Micromhos @ 25°C	1,280.	482.	26	150.	1,900.

TABLE VII

STATISTICAL ANALYSIS OF AMD

Norton Site - Stream G-1

No.	Item	Mean	Standard Deviation	Population	Minimum	Maximum
1.	Flow CFS	5.80	6.31	50	0.76	23.0
	GPM	2,590.	2,830.	-	341.	10,300.
	MMGPD	3.74	4.10	-	0.50	14.9
2.	pH	2.80	0.20	50	2.50	3.30
3.	ACIDITY as ppm $CaCO_3$	632.	141.	50	204.	890.
4.	Fe total, ppm	105.	26.5	50	35.0	160.
5.	Fe^{+2}, ppm	4.13	1.43	22	2.00	7.20
6.	SO_4^{-2}, ppm	990.	246.	50	410.	1,650.
7.	HARDNESS as ppm $CaCO_3$	449.	114.	50	167.	744.
8.	Ca^{+2}, as ppm $CaCO_3$	312.	42.5	14	243.	380.
9.	Ca^{+2}/HARDNESS	0.70	0.10	14	0.60	0.80
10.	Mg^{+2}, as ppm $CaCO_3$	137.	71.1	By Difference	-	364.
11.	Al^{+3}, ppm	41.5	6.40	13	29.	51.0
12.	CONDUCTIVITY, Micromhos @ 25°C	1,700.	326.	50	918.	2,250.

TABLE VIII

STATISTICAL ANALYSIS OF AMD

Hollywood Site

Proctor 1

No.	Item	Mean		Standard Deviation		Population	Minimum		Maximum	
		Equivalents	ppm	Equivalents	ppm		Equivalents	ppm	Equivalents	ppm
1.	pH	-	3.42	-	0.20	15	-	3.72	-	3.13
2.	Acidity	-	462.	-	150.	15	-	142.	-	671.
3.	Iron as Fe^{+2}	.0028	77.7	.0009	24.7	15	.0011	30.0	.0043	119.
4.	Aluminum (Al^{+3})	.0096	86.2	.0040	36.0	15	.0014	13.0	.0170	153.
5.	Sulfate ($SO_4^{=}$)	.0167	802.	.0054	260.	15	.0052	251.	.0247	1,190.
6.	Difference as Ca^{++}	.0043	86.0	.0005	10.0	-	.0027	54.0	-	-
7.	Conductivity, Micromhos @ 20°C	-	1,550.	-	44.6	5	-	1,520.	-	1,620.

TABLE IX

STATISTICAL ANALYSIS OF AMD

Hollywood Site

Proctor 2

No.	Item	Mean		Standard Deviation		Population	Minimum		Maximum	
		Equivalents	ppm	Equivalents	ppm		Equivalents	ppm	Equivalents	ppm
1.	pH	-	3.25	-	0.10	15	-	3.41	-	3.10
2.	Acidity	-	2,640.	-	946.	15	-	1,280.	-	5,740.
3.	Iron as Fe^{+2}	.0305	853.	.0107	298.	15	.0114	317.	.0631	1,760.
4.	Aluminum (Al^{+3})	.0279	251.	.0117	105.	15	.0185	166.	.0689	620.00
5.	Sulfate ($SO_4^{=}$)	.0724	3,480.	.0189	910.	15	.0466	2,240.	.1337	6,420.
6.	Difference as Ca^{++}	.0140	2.81	.0035	70.0	-	-	-	-	-
7.	Conductivity, Micromhos @ 20°C	-	3,590.	-	2,310.	5	-	3,190.	-	3,770.

TABLE X

STATISTICAL ANALYSIS OF AMD

Hollywood Site

Tyler Run, Pa.

No.	Item	Mean		Standard Deviation		Population	Minimum		Maximum	
		Equivalents	ppm	Equivalents	ppm		Equivalents	ppm	Equivalents	ppm
1.	pH	-	3.50	-	0.17	15	-	3.75	-	3.20
2.	Acidity	-	149.0	-	75.0	15	-	65.0	-	287.
3.	Iron as Fe^{+2}	.00005	1.50	.00003	0.90	15	.00002	0.50	.0001	3.0
4.	Aluminum (Al^{+3})	.0040	35.6	.0026	23.5	15	.001	9.00	.0098	88.0
5.	Sulfate ($SO_4^{=}$)	.0064	309.	.0032	156.	15	.0027	132.	.0123	590.
6.	Difference as Ca^{++}	.00235	47.0	.00057	11.0	-	.0017	34.0	-	-
7.	Conductivity, Micromhos @ 20°C	-	922.	-	146.	5	-	679.	-	1,040.

TABLE XI

STATISTICAL ANALYSIS OF AMD

Hollywood Site
Bennett's Branch, Pa.

No.	Item	Mean		Standard Deviation		Population	Minimum		Maximum	
		Equivalents	ppm	Equivalents	ppm		Equivalents	ppm	Equivalents	ppm
1.	pH	-	3.80	-	0.50	15	-	4.73	-	3.03
2.	Acidity	-	179.	-	143.	15	-	31.0	-	462.
3.	Iron as Fe^{+2}	.0011	30.3	.0006	17.6	15	.0003	7.00	.0021	59.0
4.	Aluminum (Al^{+3})	.0034	30.7	.0025	22.6	15	.0006	5.00	.0097	87.0
5.	Sulfate ($SO_4^{=}$)	.0062	296.	.0048	230.	15	.0013	61.0	.0156	747.0
6.	Difference as Ca^{++}	.0017	34.0	.0017	34.0	-	.0005	9.00	.0038	76.0
7.	Conductivity, Micromhos @ 20°C	-	912.	-	480.	5	-	376.	-	1,340.

TABLE XII

STATISTICAL ANALYSIS OF AMD

Hollywood Site

Stream Combination No. 1

No.	Item	Mean		Standard Deviation		Population	Minimum		Maximum	
		Equivalents	ppm	Equivalents	ppm		Equivalents	ppm	Equivalents	ppm
1.	pH	-	3.34	-	0.20	6	-	3.50	-	3.20
2.	Acidity	-	459.	-	99.0	6	-	359.	-	572.
3.	Iron as Fe^{+2}	.0025	71.0	.0009	25.0	6	.0012	33.0	.0034	96.0
4.	Aluminum (Al^{+3})	.0104	94.0	.0024	22.0	6	.0070	63.0	.0131	118.
5.	Sulfate ($SO_4^{=}$)	.0178	857.0	.0039	187.	6	.0141	679.	.0223	1,070
6.	Difference as Ca^{++}	.0049	98.0	.0006	12.0	-	-	-	-	-
7.	Conductivity, Micromhos @ 20°C	-	1,350.	-	243.	5	-	1,040.	-	1,580.

TABLE XIII

STATISTICAL ANALYSIS OF AMD

Hollywood Site

Stream Combination No. 2

No.	Item	Mean		Standard Deviation		Population	Minimum		Maximum	
		Equivalents	ppm	Equivalents	ppm		Equivalents	ppm	Equivalents	ppm
1.	pH	-	3.35	-	0.3	6	-	3.80	-	3.1
2.	Acidity	-	302.	-	165.	6	-	120.	-	543.
3.	Iron as Fe^{+2}	.0014	38.0	.0007	19.0	6	.0006	16.0	.0026	72.0
4.	Aluminum (Al^{+3})	.0062	56.0	.0036	32.0	6	.0039	35.0	.0128	115.
5.	Sulfate ($SO_4^{=}$)	.0114	549.	.0065	310.	6	.0051	245.	.0210	1,010.
6.	Difference as Ca^{++}	.0038	76.0	.0022	44.0	-	.0006	12.0	-	-
7.	Conductivity, Micromhos @ 20°C	-	1,020.	-	438.	5	-	570.	-	1,550.

TABLE XIV

STATISTICAL ANALYSIS OF AMD
Hollywood Site
Composite(*)

No.	Item	Mean		Standard Deviation		Population	Minimum		Maximum	
		Equivalents	ppm	Equivalents	ppm		Equivalents	ppm	Equivalents	ppm
1.	pH	-	3.5	-	0.34	63	-	4.74	-	2.90
2.	Acidity	-	954.	-	1,450.	63	-	31.0	-	8,110.
3.	Iron as Fe^{+2}	.013	354.	.026	720.	63	.00002	0.50	.166	4,620.
4.	Aluminum (Al^{+3})	.011	101.	.012	106.	62	.0006	5.00	.069	620.
5.	Sulfate ($SO_4^{=}$)	.025	1,220.	.029	1,410.	62	.001	61.0	.134	6,420.
6.	Difference as Ca^{++}	.002	30.	-	-	-	.0007	14.0	-	-
7.	Conductivity, Micromhos @ 20°C	-	1,660.	-	1,040.	25	-	376.0	-	3,770.

(*) Data includes 1 point (6/10 data) not included in separate stream analyses; this point is an extreme case and has caused the high standard deviations occurring in this composite.

APPENDIX B

PRETREATMENT TESTS

TABLE XV

Summary of Pretreatment Tests

Run Number	610B	610D	613A	613B	613C	613D	616A	616B	616C
Initial pH	2.0	2.0	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Initial Iron, ppm	1156.	1156.	1156.	1156.	1156.	1156.	1156.	1156.	1156.
Initial Aluminum, ppm	85.	85.	85.	85.	85.	85.	85.	85.	85.
Initial Calcium, ppm	280.	280.	-	-	-	-	280.	280.	280.
Soda Ash Added, gm	1.752	1.684	1.733	2.240	1.773	1.910	1.78	1.88	1.99
Immediate pH	5.0	5.0	5.0	6.1	5.0	5.6	-	-	-
Stoichiometric Amount, gm	1.85	1.85	1.85	1.85	1.85	1.85	1.85	1.85	1.85
Actual/Stoichiometric	0.95	0.91	0.94	1.21	0.96	1.05	1.09	1.15	1.22
Mixing Time, hrs.	0.5	0.5	2.	2.	2.	2.	2.	2.	2.
End pH	-	-	5.3	7.3	5.6	6.4	-	-	-
Sparging Time, hrs.	-	0.5	-	-	0.5	0.5	0.5	-	0.5
End pH	-	-	-	-	-	-	-	-	-
Settling Time, hrs.	2.	2.	2.	2.	2.	2.	2.	2.	2.
End pH	-	-	5.4	7.6	6.5	7.0	4.85	6.40	7.00
Analytical Results									
pH	5.8	4.7	5.1	8.0	6.6	7.35	4.4	6.5	7.0
Bicarbonate, ppm	55.	33.	20.	642.	20.	80.	57.	97.	142.
Total Iron, ppm @ Top	11.2	41.9	14.0	1.6	1.1	2.4	43.6	2.13	2.07
Total Iron, ppm @ Bottom	14.5	45.4	18.3	1.9	1.6	2.5	44.8	6.71	3.24
Dissolved Iron, ppm	9.0	39.5	11.7	0.37	0.25	0.13	41.1	1.14	0.38
Total Aluminum, ppm	1.14	1.04	1.57	0.64	0.78	1.47	2.59	1.01	0.59
Dissolved Aluminum, ppm	-	-	0.88	0.20	0.15	0.05	2.45	0.92	0.39
Total Calcium, ppm	260.	280.	-	-	-	-	284.	272.	248.
Dissolved Calcium, ppm	-	-	-	-	-	-	280.	264.	244.
Sludge Volume, cc	150.	155.	177.	180.	165.	125.	167.	165.	167.

TABLE XV

Summary of Pretreatment Tests (Cont'd)

Run Number	616D	616E	616F	619A	619B	619C	619D	619E	620A
Initial pH	2.1	2.1	2.1	2.0	2.0	2.0	2.0	2.0	2.43
Initial Iron, ppm	1156.	1156.	1156.	1156.	1156.	1156.	1156.	1156.	120.
Initial Aluminum, ppm	85.	85.	85.	85.	85.	85.	85.	85.	-
Initial Calcium, ppm	280.	280.	280.	-	-	-	-	-	-
Soda Ash Added, gm	2.45	2.22	2.58	1.773	1.773	1.815	1.910	1.910	0.210
Immediate pH	-	6.0	6.4	4.95	5.35	5.33	5.40	5.41	5.38
Stoichiometric Amount, gm	1.85	1.85	1.85	1.85	1.85	1.85	1.85	1.85	0.171
Actual/Stoichiometric	1.50	1.36	1.58	0.96	0.96	0.98	1.03	1.03	0.84
Mixing Time, hrs.	2.	2.	2.	2.	1.	1.	2.	2.	2.
End pH	-	7.12	7.77	5.57	5.43	5.72	6.78	6.95	5.39
Sparging Time, hrs.	-	0.5	-	0.5	0.5	0.5	0.5	0.5	0.5
End pH	-	-	-	5.52	5.55	6.07	7.0	7.3	5.52
Settling Time, hrs.	2.	2.	2.	2.	2.	2.	2.	2.	2.
End pH	7.7	7.9	8.3	6.3	5.8	6.6	-	-	4.88
Analytical Results									
pH	7.5	7.6	7.8	6.2	5.9	6.6	7.85	7.85	5.0
Bicarbonate, ppm	801.	393.	1015.	39.	34.	97.	302.	312.	74.
Total Iron, ppm @ Top	1.03	1.27	0.70	2.18	10.4	1.65	3.76	3.27	11.3
Total Iron, ppm @ Bottom	2.09	2.17	1.88	5.3	17.6	3.91	4.58	5.37	13.2
Dissolved Iron, ppm	0.25	0.44	0.28	0.20	5.20	0.50	0.21	0.41	7.7
Total Aluminum, ppm	0.43	0.48	0.42	0.79	2.16	0.73	0.64	0.47	-
Dissolved Aluminum, ppm	0.14	0.24	0.22	0.08	0.22	0.05	0.13	0.09	-
Total Calcium, ppm	188.	192.	140.	-	-	-	-	-	-
Dissolved Calcium, ppm	188.	192.	136.	-	-	-	-	-	-
Sludge Volume, cc	185.	165.	182.	105.	136.	145.	125.	95.	25.

TABLE XV

Summary of Pretreatment Tests (Cont'd)

Run Number	620B	620C	620D	623A	623B	623C	623D	702	703
Initial pH	2.45	2.36	2.37	2.44	2.47	2.36	2.35	2.32	2.40
Initial Iron, ppm	120.	120.	NORTON	NORTON	NORTON	117.	117.	NORTON	NORTON
Initial Aluminum, ppm	35.	35.	FEED-	FEED-	FEED-	-	35.	FEED-	FEED-
Initial Calcium, ppm	-	100.	WATER	WATER	WATER	-	100.	WATER	WATER
Soda Ash Added, gm	0.306	0.305	0.283	0.290	0.290	0.247	0.334	0.508	0.319
Immediate pH	5.38	5.36	5.45	5.68	5.67	5.75	5.65	7.05	5.75
Stoichiometric Amount, gm	0.255	0.255	-	-	-	0.167	0.250	-	-
Actual/Stoichiometric	1.22	1.22	-	-	-	1.48	1.33	-	-
Mixing Time, hrs.	2.	2.	2.	0.5	0.5	2.	2.	2.	2.
End pH	5.50	-	-	5.89	5.94	6.82	6.52	8.51	6.54
Sparging Time, hrs.	0.5	0.5	0.5	0.25	-	0.5	0.5	0.5	0.5
End pH	5.86	6.17	6.5	6.33	-	6.95	6.62	8.52	6.45
Settling Time, hrs.	2.	2.	2.	2.	2.	2.	2.	2.	2.
End pH	5.36	5.97	6.33	6.43	5.9	7.02	6.84	8.39	5.05
Analytical Results									
pH	5.6	6.2	6.4	6.9	6.45	7.20	7.1	8.3	6.8
Bicarbonate, ppm	79.	72.	76.	130.	135.	142.	125.	1221.	121.
Total Iron, ppm @ Top	8.6	4.2	3.4	-	-	-	-	-	-
Total Iron, ppm @ Bottom	9.1	4.0	4.1	1.1	2.7	4.25	3.57	3.07	3.69
Dissolved Iron, ppm	5.9	0.79	0.77	0.55	0.94	0.25	0.73	0.09	0.48
Total Aluminum, ppm	0.98	1.09	1.50	0.80	1.72	-	0.24	1.10	0.44
Dissolved Aluminum, ppm	0.68	0.38	0.21	0.30	0.48	-	0.38	0.41	.005
Total Calcium, ppm	-	96.	136.	132.	140.	-	120.	104.	105.
Dissolved Calcium, ppm	-	96.	136.	132.	144.	-	112.	104.	112.
Sludge Volume, cc	25.	25.	25.	35.	25.	20.	35.	50.	25.

TABLE XVI

SLUDGE SETTLING TESTS

Cubic Centimeters Occupied By Sludge At Interface

Run Number	Time, Minutes 0	5	10	20	30	40	50	60	120
610B	510	495	455	392	327	280	245	215	150
610D	510	-	460	382	284	240	244	210	162
613A	500	495	485	431	380	330	288	254	177
613B	500	493	486	433	370	315	271	237	168
613C	500	488	460	399	342	290	250	225	165
613D	500	-	453	286	214	180	165	155	125
616A	505	477	427	377	335	292	255	231	167
616B	510	502	465	405	345	285	246	220	165
616C	510	480	412	345	292	255	230	215	167
616D	510	502	492	493	445	340	287	255	185
616E	505	497	475	395	331	275	242	225	165
616F	505	500	480	465	382	330	280	247	182
619A	500	485	428	340	282	230	200	175	105
619B	495	445	367	265	215	180	155	147	136
619C	510	500	493	405	332	270	235	205	145
619D	495	380	320	239	193	170	163	150	125
619E	495	335	195	143	125	120	110	107	95
620A	500	75	25	-	-	-	-	-	-
620B	500	100	75	50	50	-	-	-	-
620C	500	100	50	-	-	-	-	-	-
620D	500	75	25	25	25	-	-	-	-
623A	500	-	85	75	60	50	-	35	35
623B	500	140	120	75	65	50	-	25	25
623C	500	-	-	25	20	20	-	20	20
623D	500	-	100	70	55	50	-	50	35
702	500	90	75	50	50	50	50	50	50
703	505	70	70	50	45	40	35	25	25

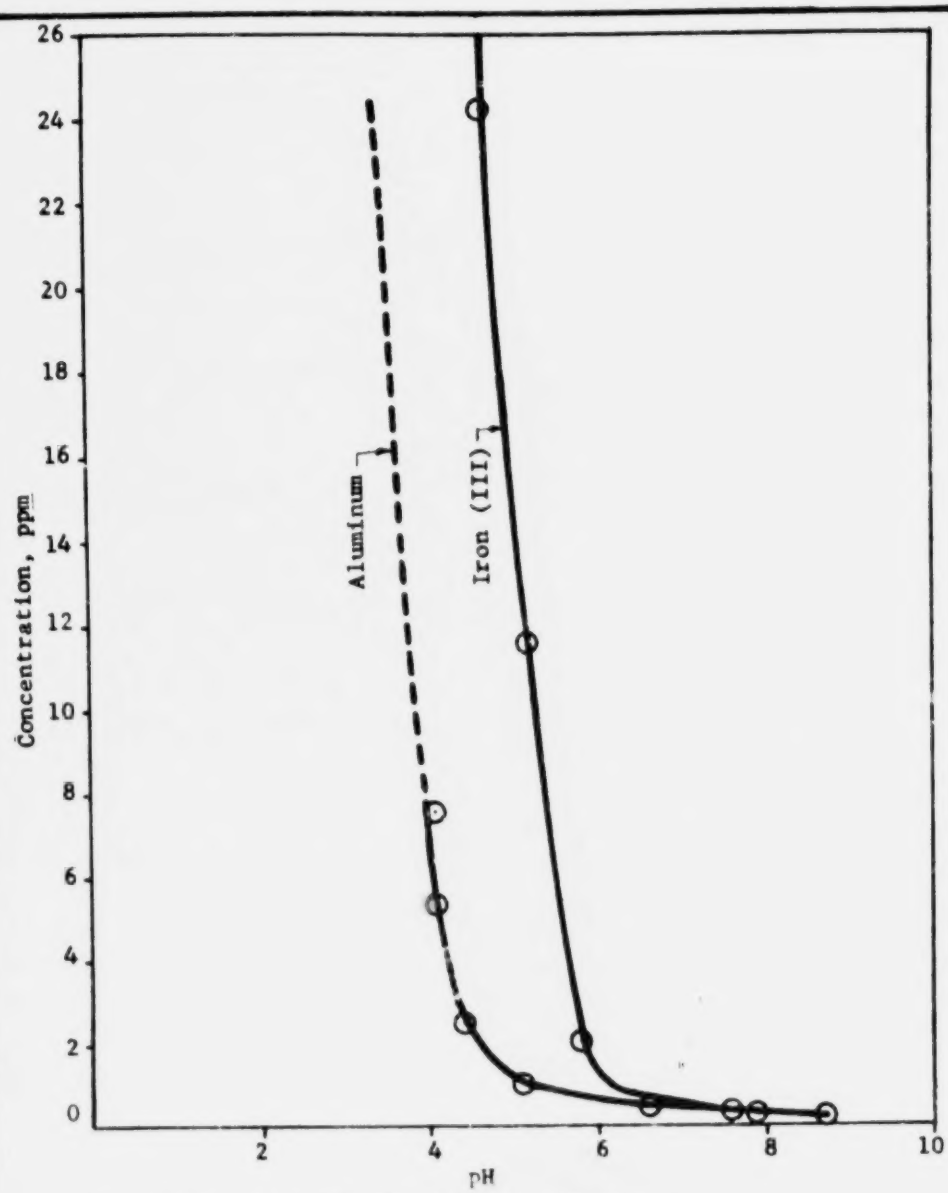

Figure 6: Iron and Aluminum in Solution after Neutralization

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FWQA Cont. 14-12-518

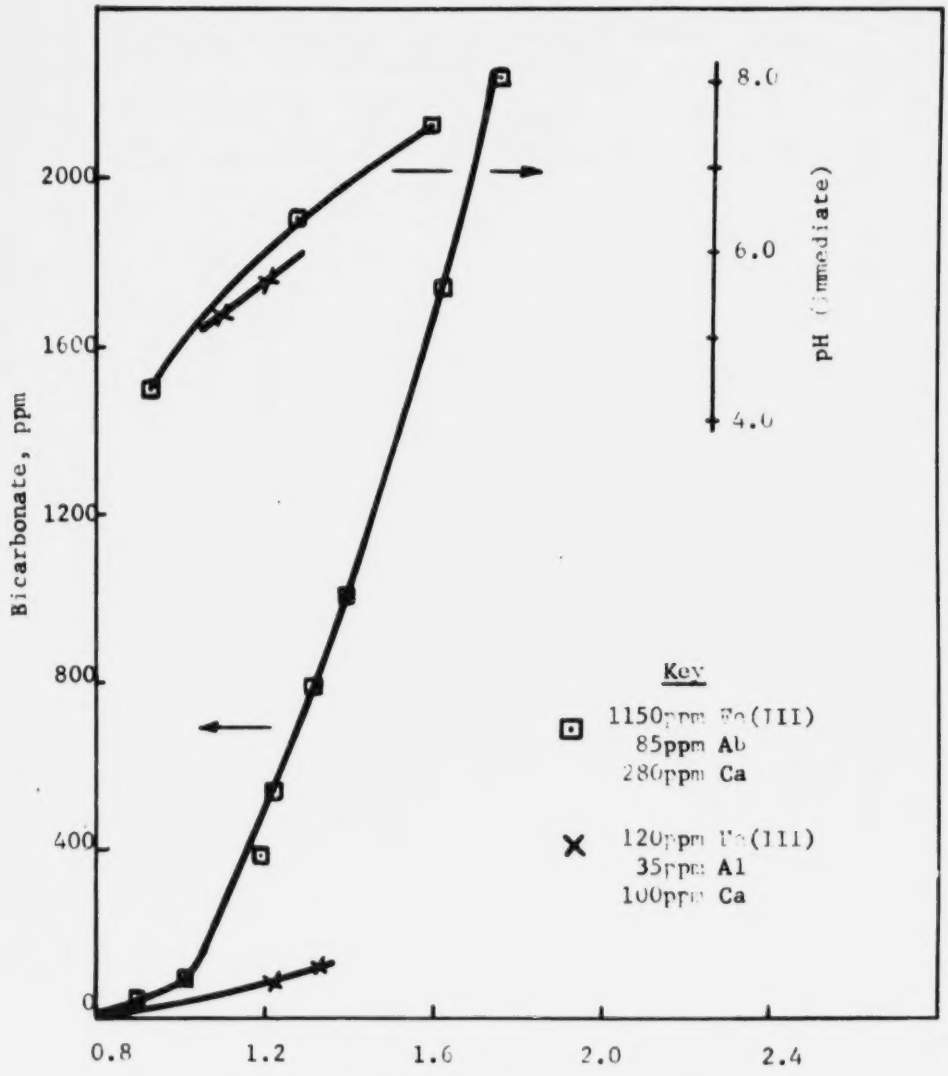

Figure 7: Bicarbonate and pH as Functions of Soda Ash Addition

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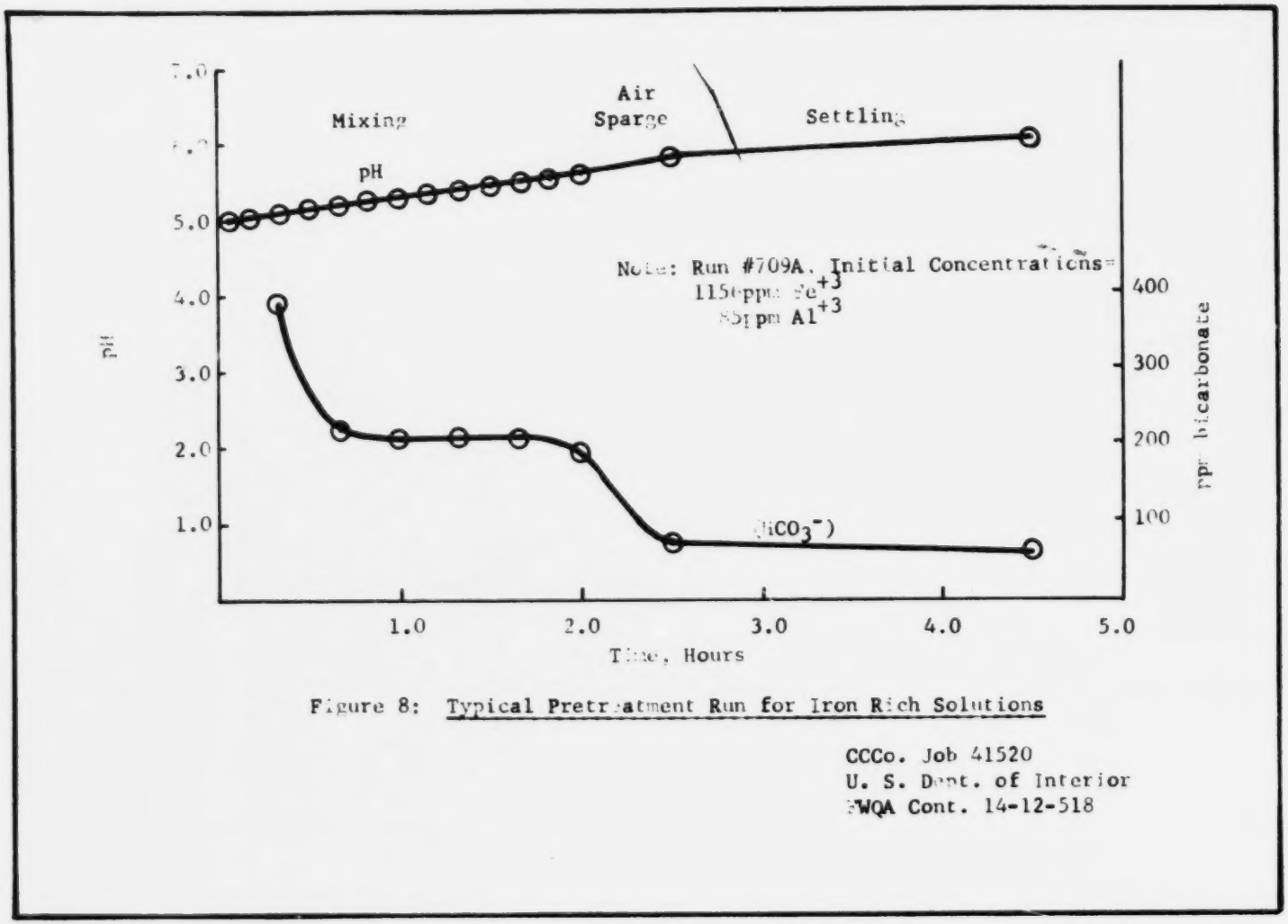

Figure 8: Typical Pretreatment Run for Iron Rich Solutions

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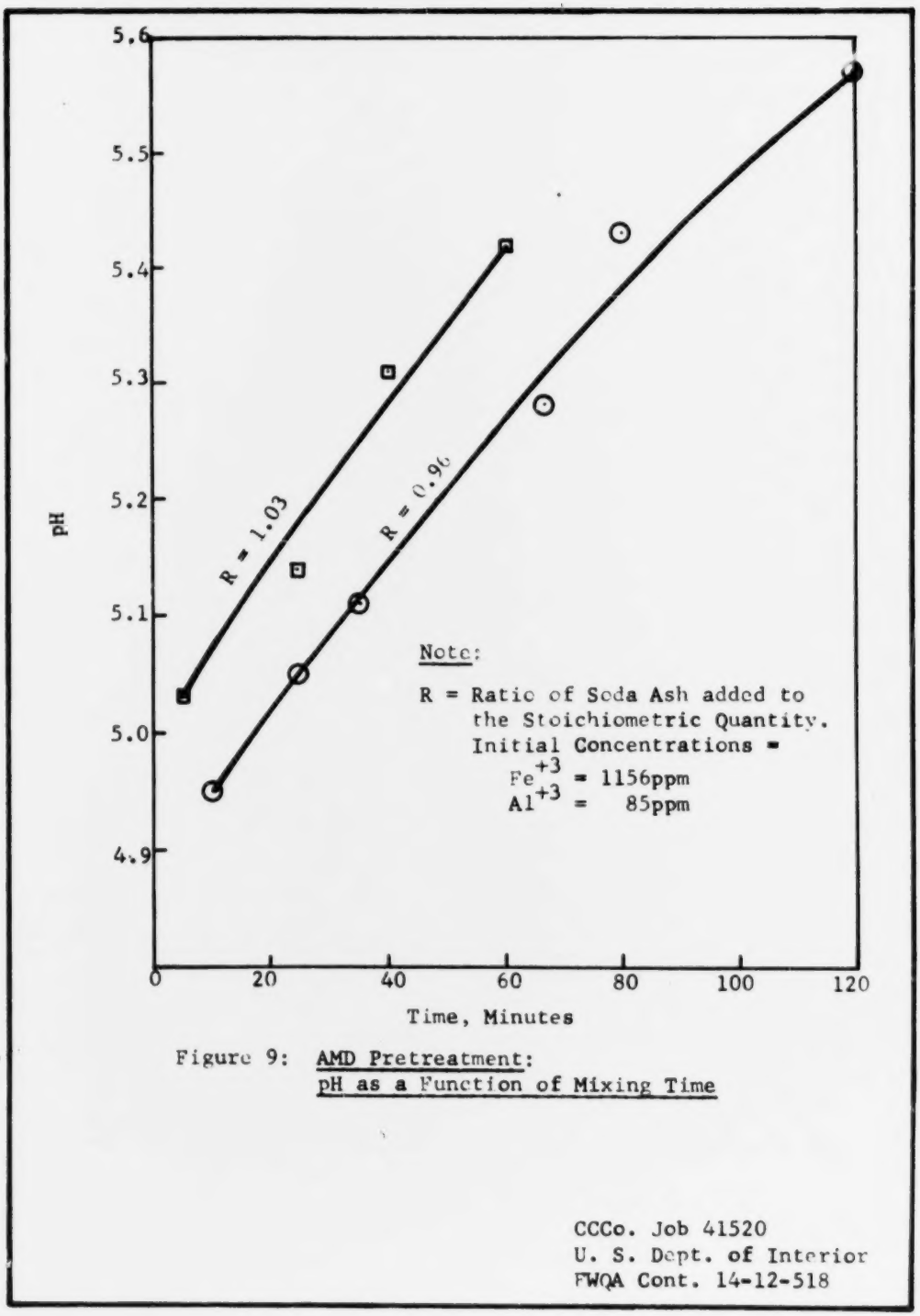

Figure 9: AMD Pretreatment:
pH as a Function of Mixing Time

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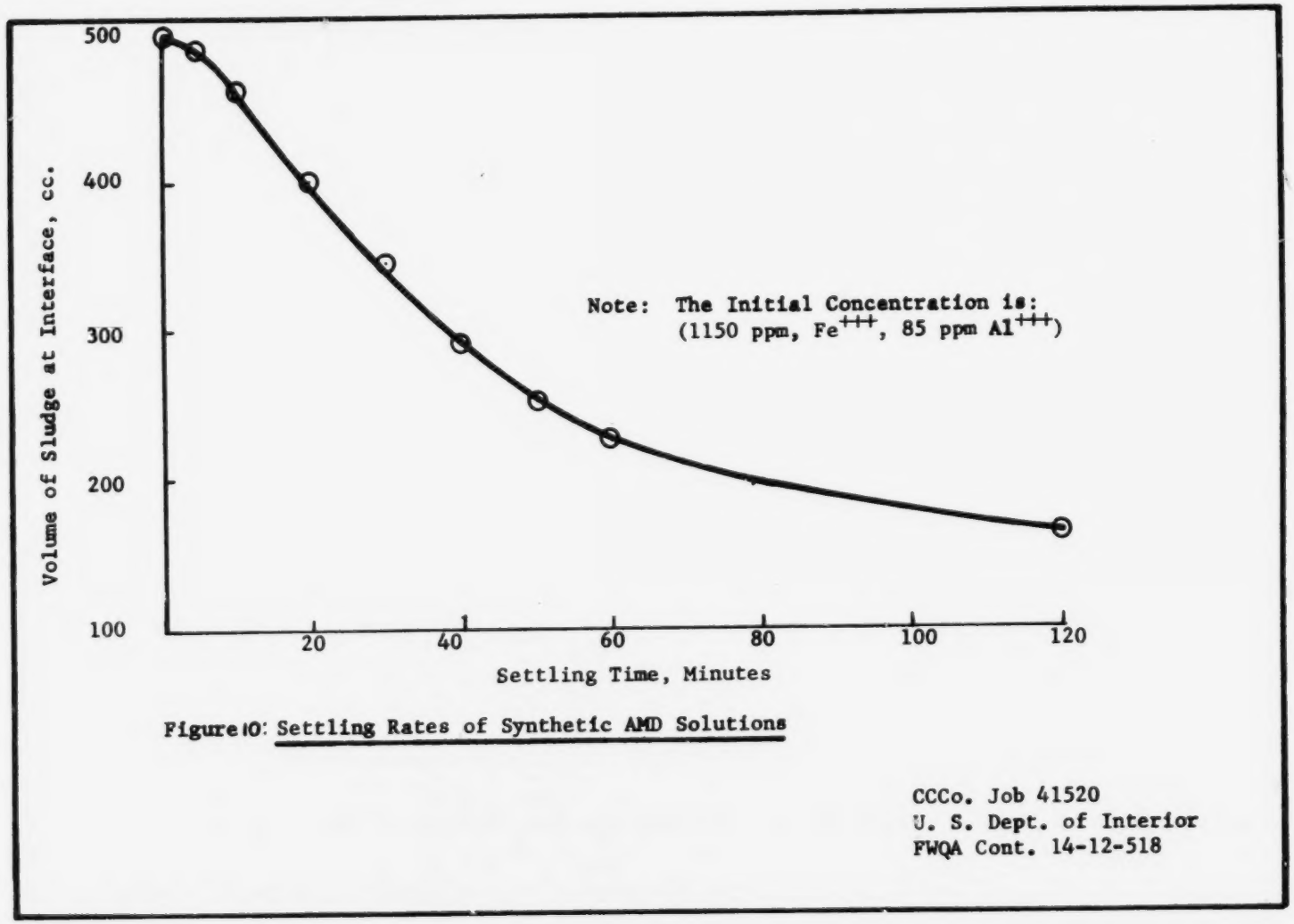

Figure 10: Settling Rates of Synthetic AMD Solutions

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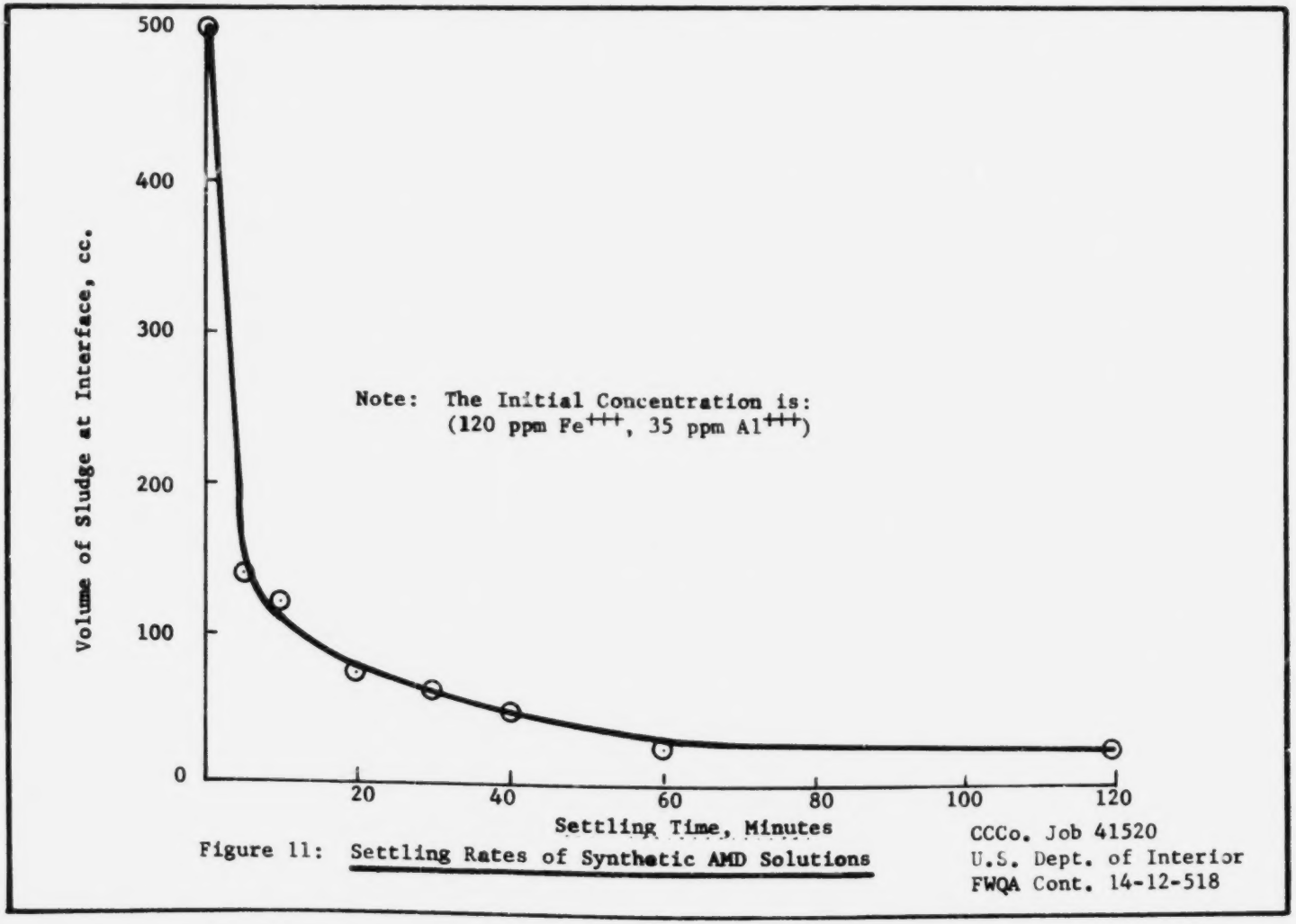

Figure 11: Settling Rates of Synthetic AMD Solutions

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APPENDIX C

BATCH ELUTION TESTS

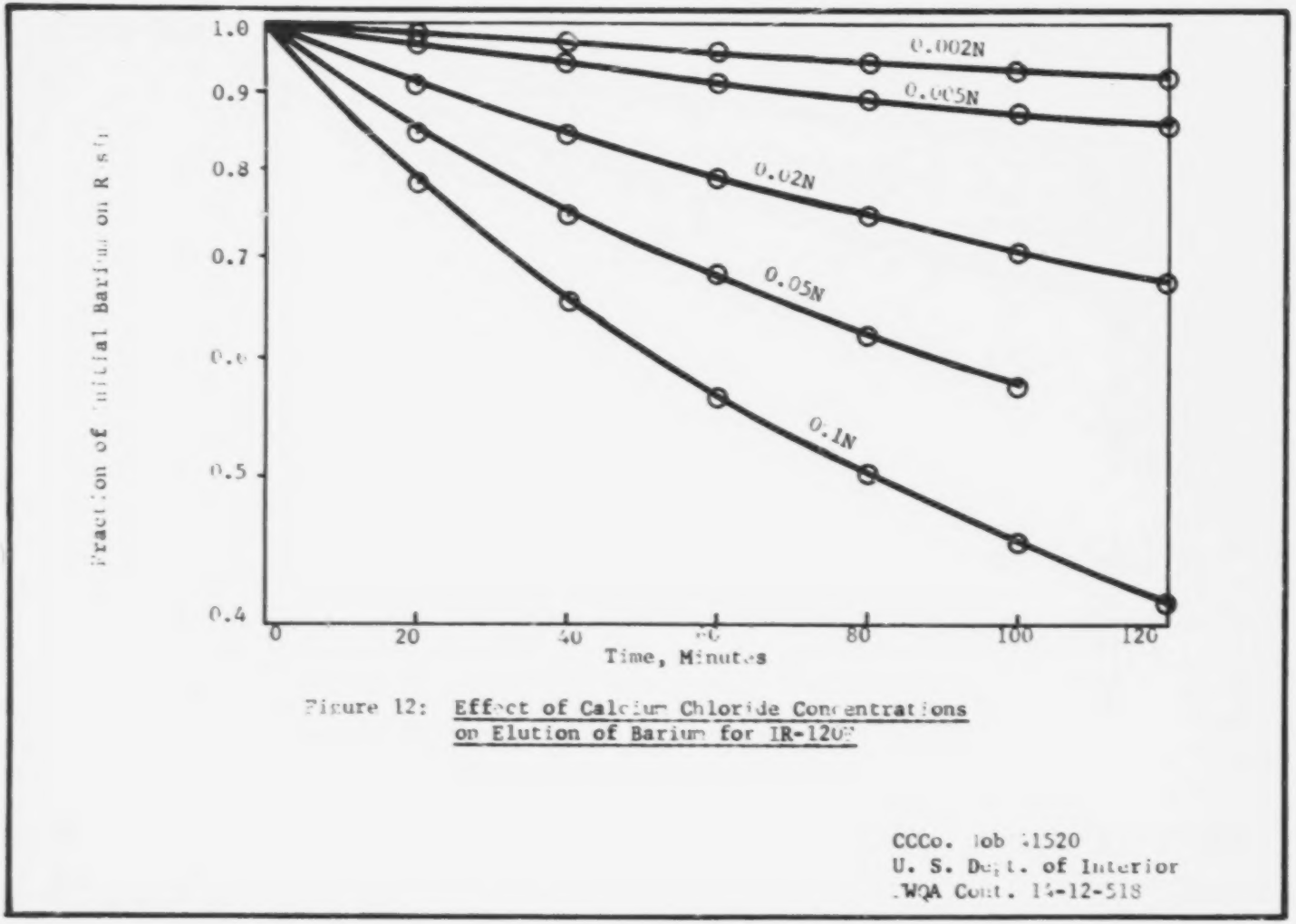

Figure 12: Effect of Calcium Chloride Concentrations on Elution of Barium for IR-120P

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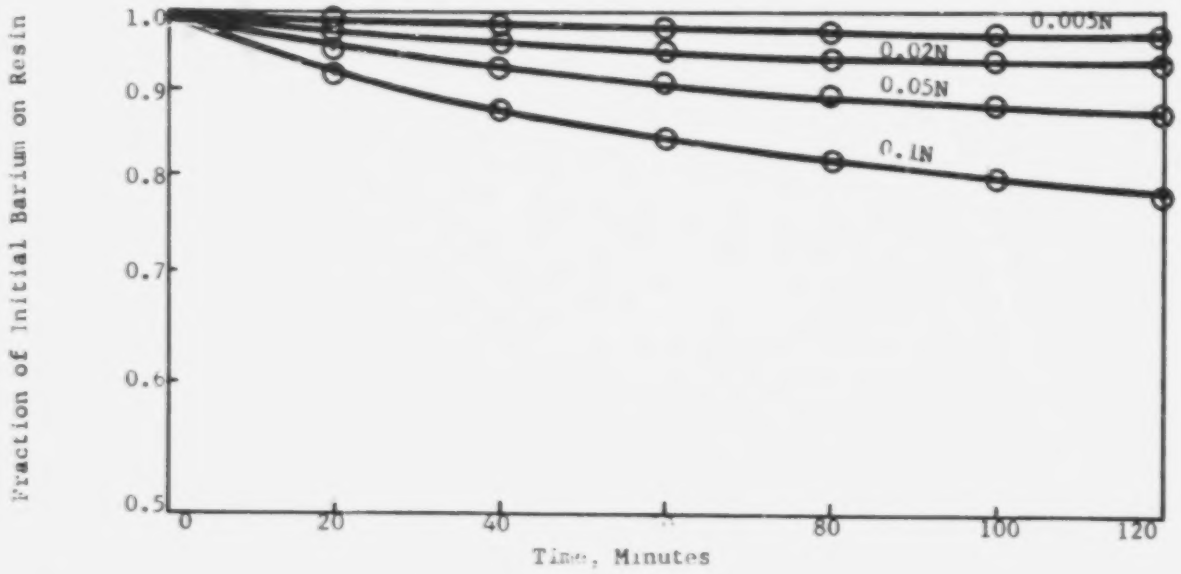

Figure 13: Effect of Sodium Chloride Concentrations on Elution of Barium for IR-120P

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WQA Cont. 14-12-518

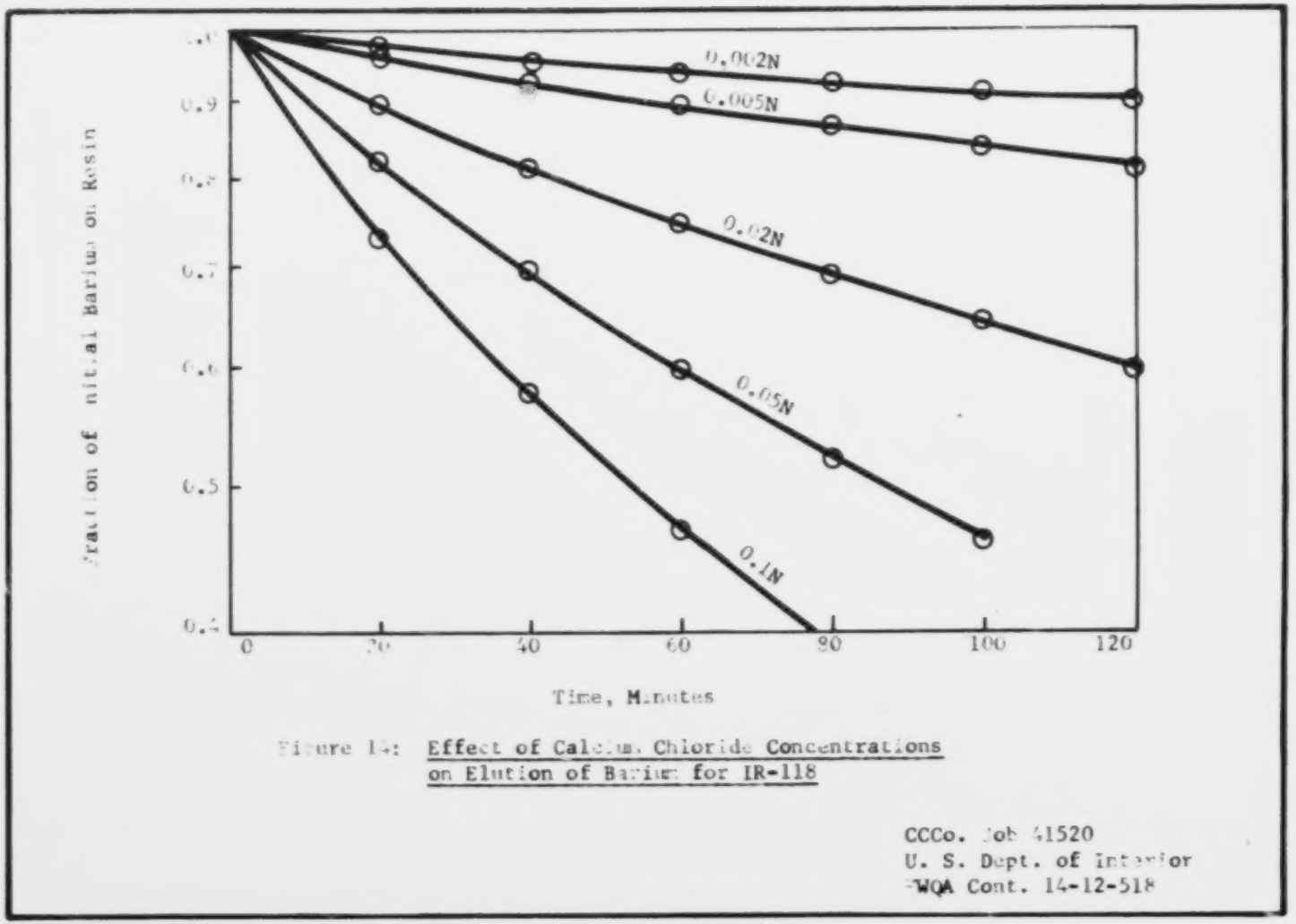

Figure 14: Effect of Calcium Chloride Concentrations on Elution of Barium for IR-118

CCCo. Job 41520
U. S. Dept. of Interior
FWQA Cont. 14-12-518

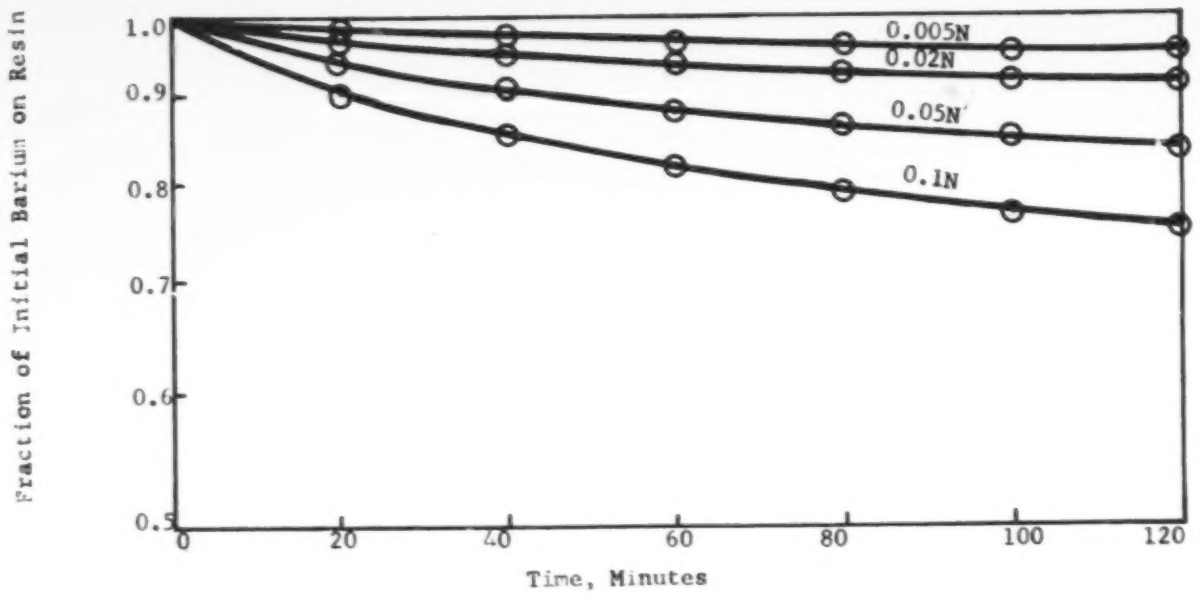

Figure 15: Effect of Sodium Chloride Concentrations on Elution of Barium for IR-118

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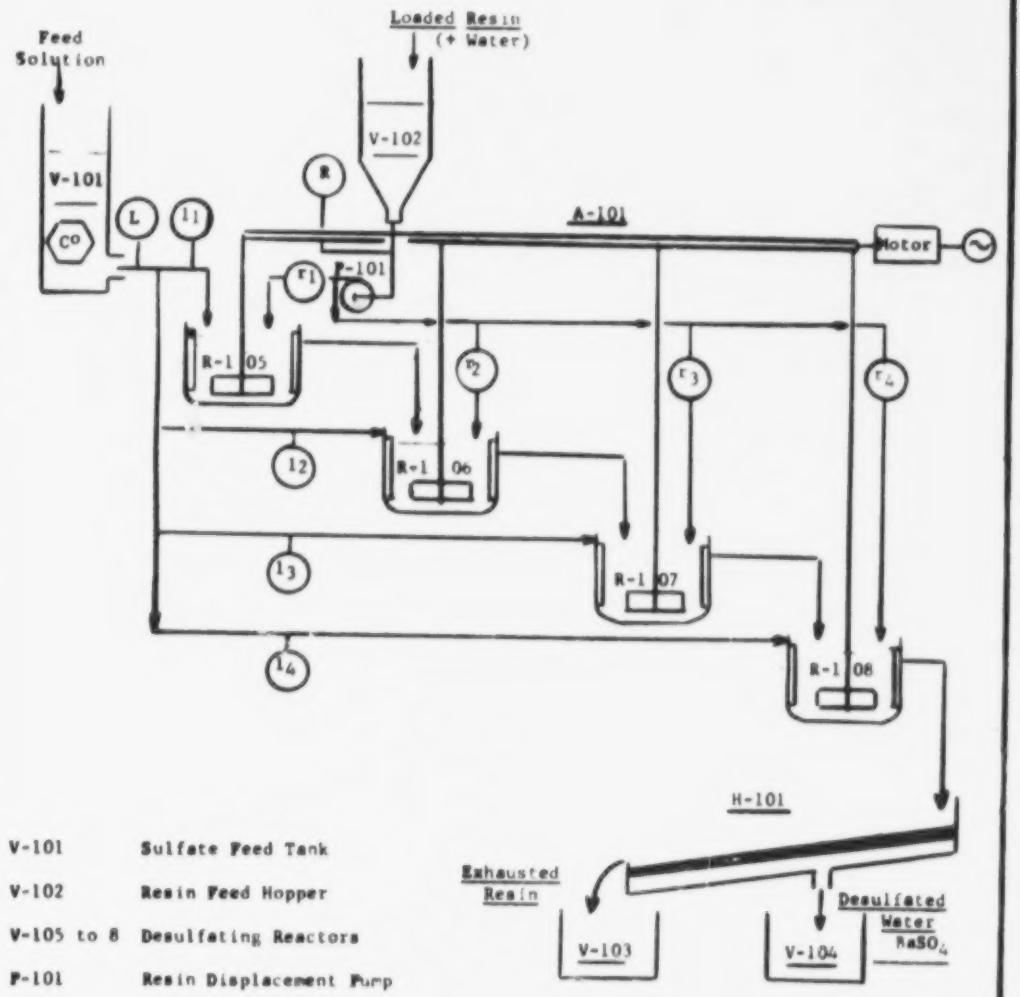
WQA Cont. 14-12-518



V-101	Sulfate Feed Tank
V-102	Resin Feed Hopper
V-105 to 8	Desulfating Reactors
P-101	Resin Displacement Pump
V-103	Spent Resin Bucket
V-104	$BaSO_4$ - water slurry bucket
H-101	Vibrating Screen
A-101	Paddle Agitators (4) - two blade

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FIGURE 16 - CONTINUOUS ION EXCHANGE DESULFATING APPARATUS

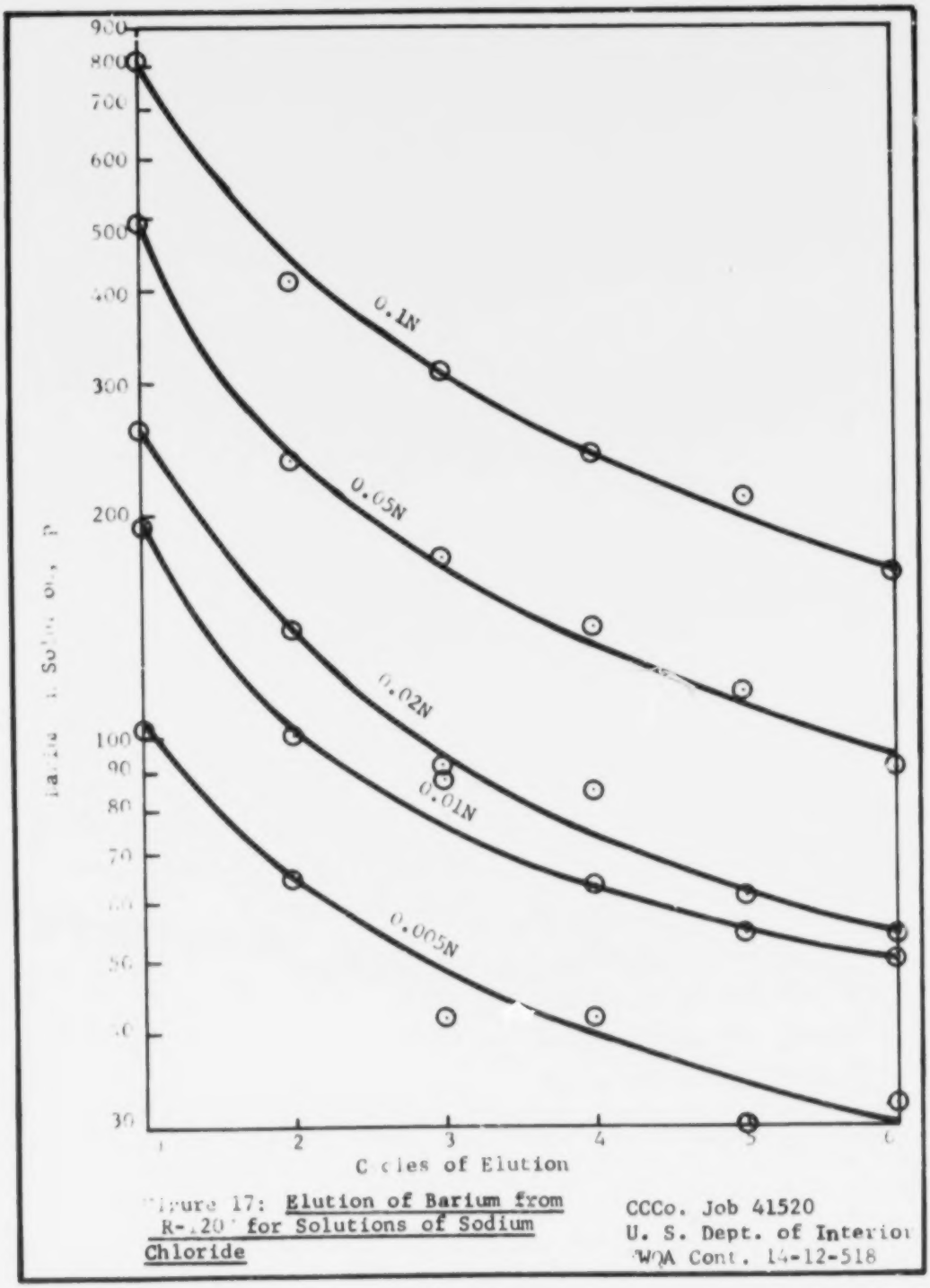

Figure 17: Elution of Barium from R-120 for Solutions of Sodium Chloride

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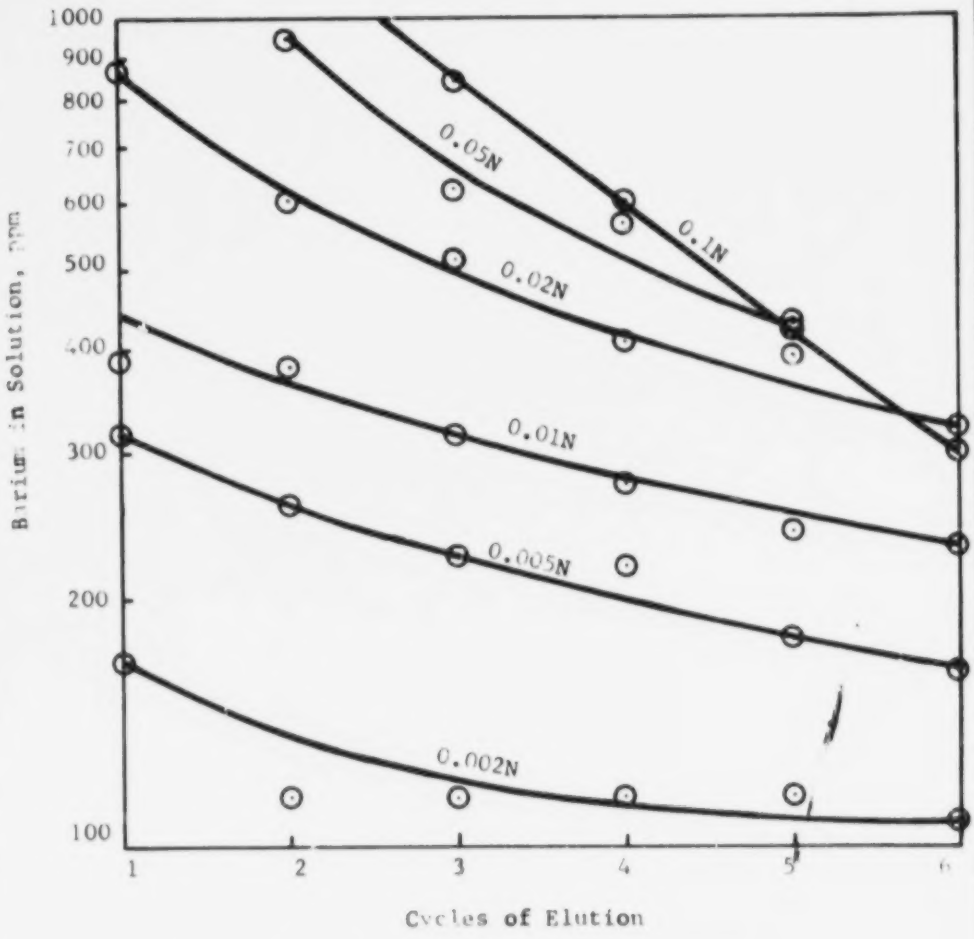

Figure 18: Elution of Barium from IR-120 for Solutions of Calcium Chloride

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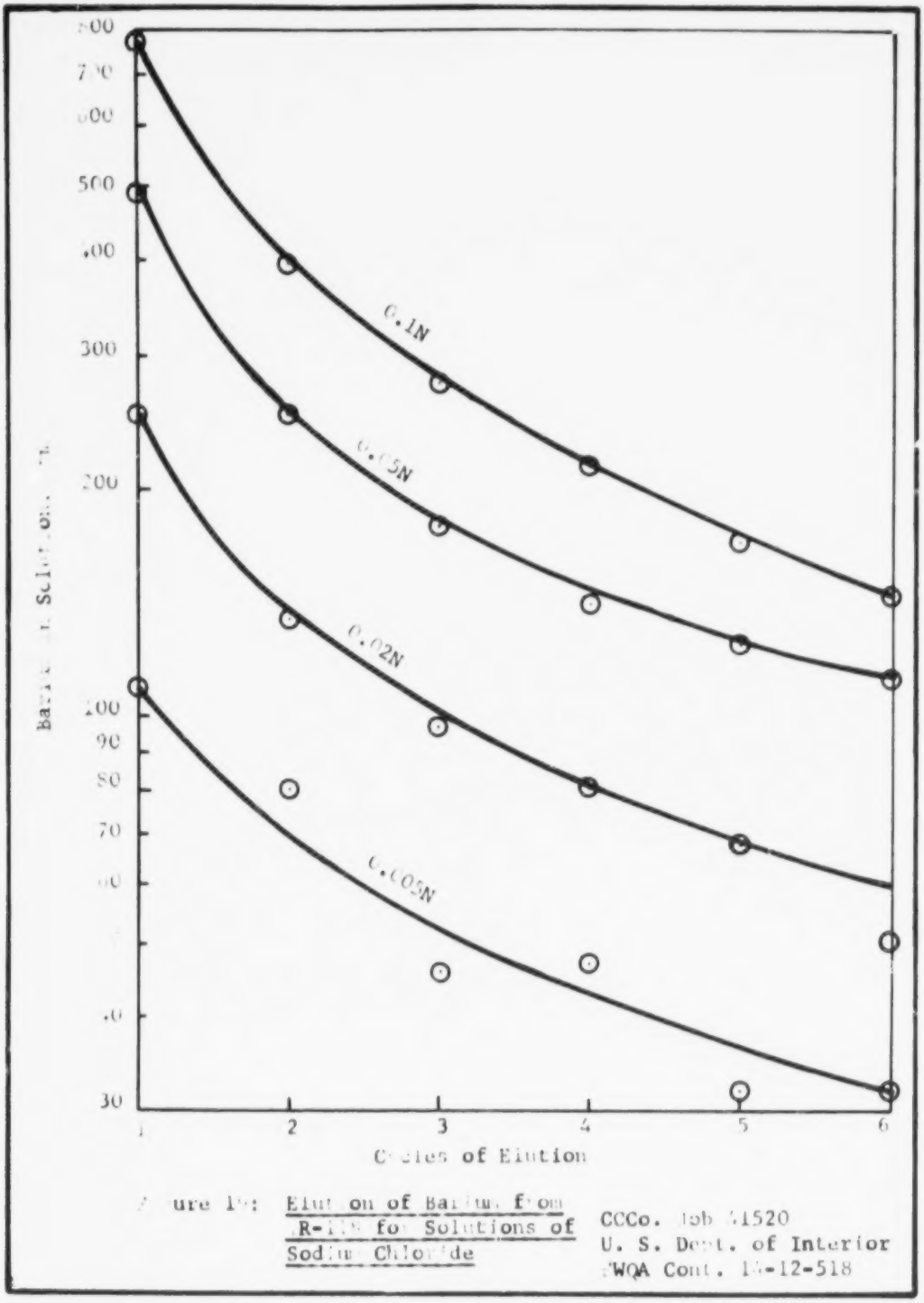

Figure 19: Elution of Barium from R-[illegible] for Solutions of Sodium Chloride

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U. S. Dept. of Interior
WQA Cont. 14-12-518

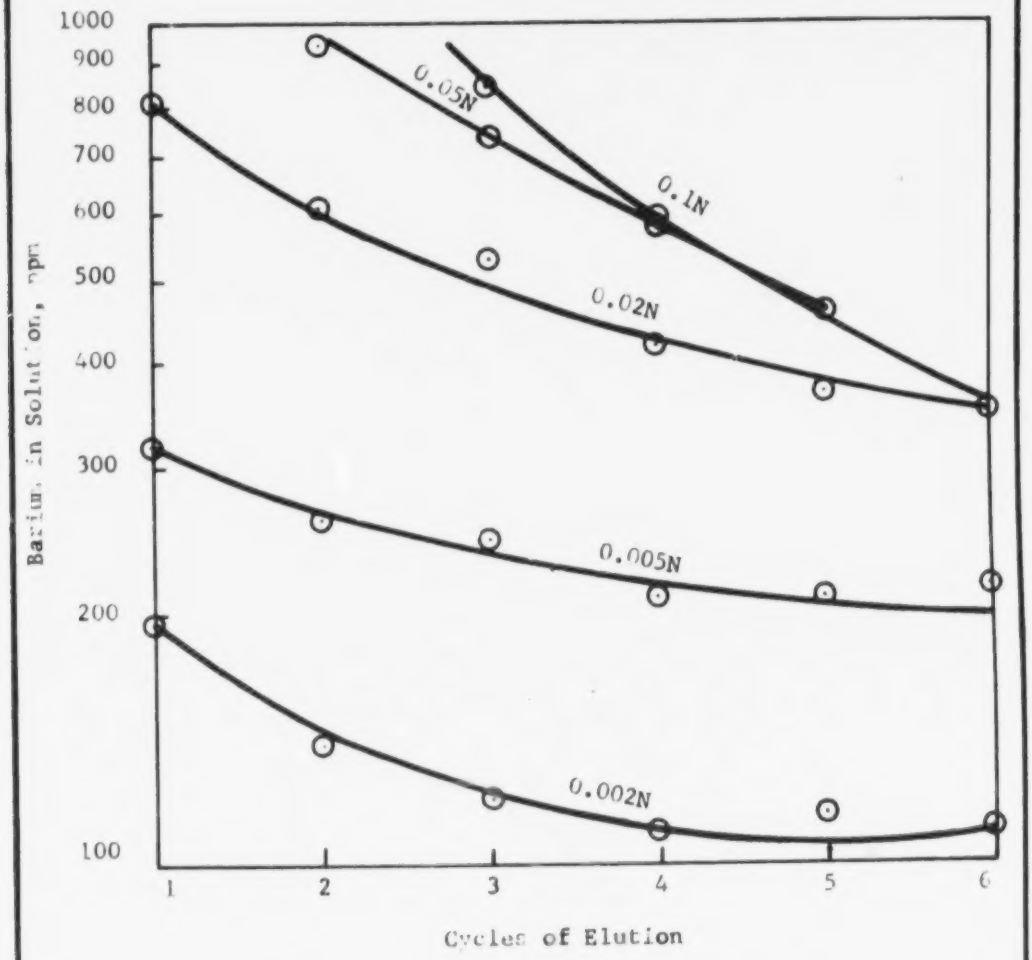

Figure 20: Elution of Barium from IR-118 for Solutions of Calcium Chloride

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U. S. Dept. of Interior
FWQA Cont. 14-12-518

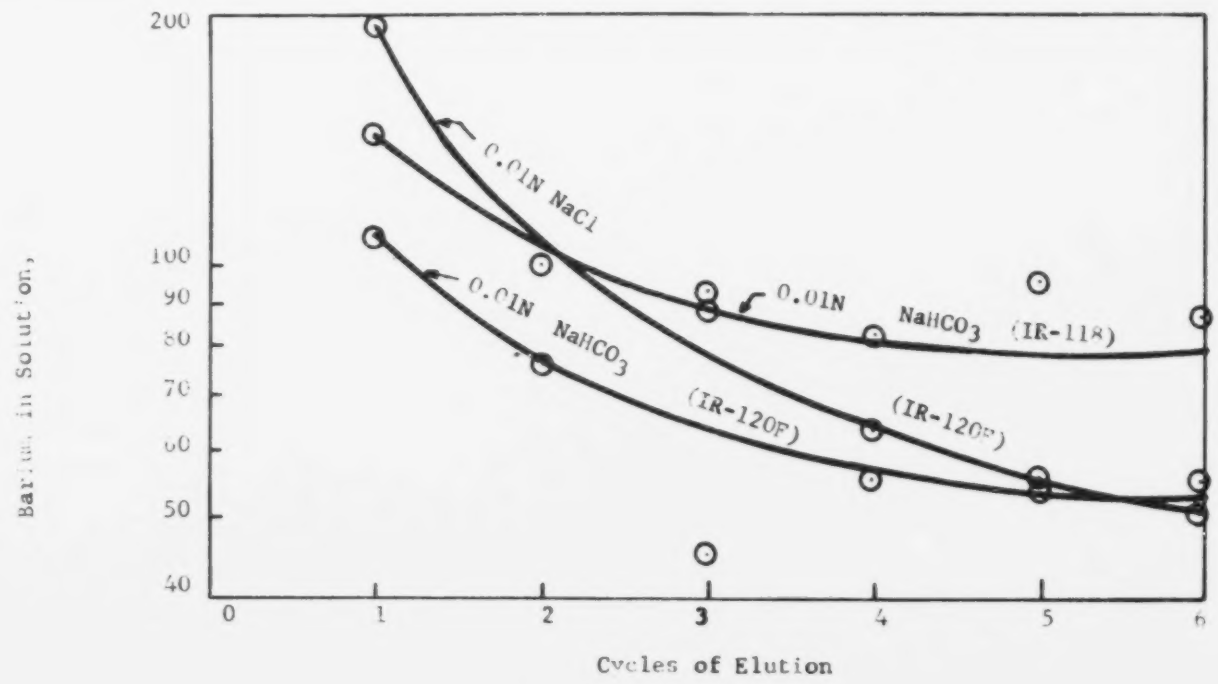

Figure 21: Effect of Anion on Elution of Barium from IR-Resins

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U. S. Dept. of Interior
FWQA Cont. 14-12-518

APPENDIX D

ONE MILLION GALLON

PER DAY PLANT

PRODUCTION PLANT - ONE MILLION GPD

PROCESS

Design Conditions

Scope:

The specified production plant is based on experience from several sources, plus additional laboratory experimentation. The AMD pretreatment and desulfating sections are based on experimental laboratory work (see page 7) conducted under the FWQA contract. The resin regeneration, effluent treatment, barium conversion, and carbonation sections are based mainly on the work conducted by the Bureau of Mines (2), and on previous Catalytic design packages (3, 4).

Basis:

The design throughput of the production plant is one million gallons per day of acid mine drainage.

The unit is designed to handle feed of the composition listed in the Appendix A, Table V, for Norton Profile, but is readily adaptable(*) to Hollywood Profile (listed in Appendix A, Tables VIII to XIII). These are statistical compilations from available data. Material balance and economics are based on the Norton Site.

The ion exchange regenerant will be an aqueous solution of 50-50 barium hydrosulfide and barium hydroxide, which has a normality of 0.1.

The production plant shall be fully automated so that it can be run continuously to satisfy commercial requirements.

The ion exchange regeneration process shall be a continuous process, attaining the maximum allowable superficial velocity through T-301 A/B Loading Columns and minimizing barium leakage into the effluent solution.

Complete removal of barium from the pore solution of the resin is required (T-302 Rinsing Column).

Attrition of ion exchange beads shall be kept to an absolute minimum throughout the production plant.

(*) Additional clarifier area is required.

The recovery of high clarity AMD from pretreatment and desulfating operations shall be maximized by use of special flocculents, reaction type gravity-settling devices, and subsequent dewatering by centrifugation. Carry over of barite fines from clarification shall be minimized and filtration shall be used to insure a clear product.

A relatively high excess of resin over the amount needed stoichiometrically for complete desulfating will be used due to low reactivity of the resin in dilute ionic solutions (laboratory results dictate use of 4x the stoichiometric quantity). A 20-30 percent exhausted resin must be regenerated, requiring use of a dilute liquor in order to minimize barium losses and effluent treating costs.

The following criteria were used in compiling a capital cost estimate for the economic evaluation.

All utilities will be made available on the premises.

Makeup regenerant in the barite form will be kept in dry storage (50-pound bags). Sulfuric acid will be stored in 42-gallon barrels. Sodium chloride (Salt Cake) shall be stored in a lixator vessel which generates a saturated solution to the process. Flocculent for both pretreatment and desulfating will be received and stored in bags. Makeup resin will be purchased and kept in dry storage containers. Storage capacity will be for two week production periods for all chemicals, and for sulfur by-product.

A laboratory and equipment, operating and control room, office, maintenance, and storage facilities shall be furnished.

Loading and unloading facilities and roadways shall be supplied.

The makeup filter, feed pump, and storage lixator shall be furnished with concrete bases, and the process water surge pond shall be fiberglass or polyethylene lined.

The plant, facilities, and offsites require a plot 350 x 200 feet wide, or 1.61 acres.

Process Description - Neutradesulfating AMD Process

Introduction

The process flowsheets (R-211 and R-212, Appendix D) are based on the neutradesulfating of one million gallons of acid mine drainage per day (1MM GPD). The process described here is shown in block form in Figure 22 and is a modification of the process developed by the Bureau of Mines (2). This process would provide a product which would meet interstate water quality criteria.

The production plant is a continuous, automated operation equipped with Pretreatment, Desulfating, Resin Regeneration, Effluent and Waste Treatment (drawing R-211), Barium Conversion and Carbonation Sections (drawing R-212), and By-Product Recovery(*). The desulfating section is pressurized.

Removal of Iron & Aluminum from AMD

Raw AMD is passed through a traveling water screen prior to pumping in order to remove twigs, leaves and other debris from the feed. The screen, along with the AMD feed pump, is in a concrete surge pond located in the feed stream itself. Filtered AMD is then distributed in parallel to two pretreatment reactors. Prior to entering the reactor, the AMD feed stream is injected with a dilute sodium bicarbonate solution from the Carbonation Section at a rate which is controlled by the pH of the pretreated AMD stream. After a period (generally one hour) of air sparging in vigorously agitated pretreatment reactors to insure both a complete pretreatment reaction and oxidation of all ferrous ion to ferric, the neutralized mine drainage flows by gravity into the feedwell of the pretreatment clarifier. The iron suspension is then passed into an agitated reaction zone where it is contacted with an anti-flocculent which aids in decreasing spherical interferences between the particles which can cause a colloidal state

(*) Sulfur Recovery Plant is a packaged item and the flow diagram and process description are not included here.

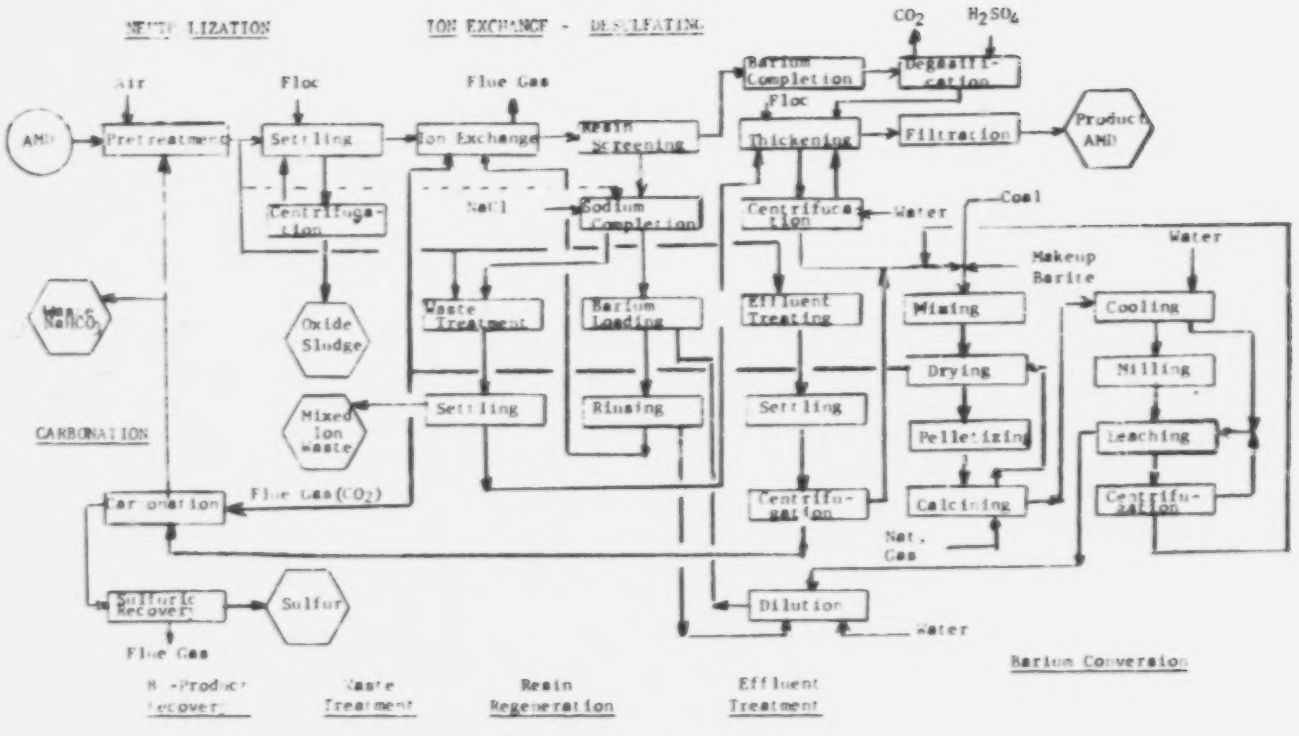

FIGURE - 22

FLOW DIAGRAM FOR AMD

NEUTRALIZATION

Federal Water Quality Administration
Contract No. 14-12-518

Cereal Tir, Inc.
Cont., 41520
Dec., 1969

to form in the system. Even with such an aid, slow, hindered settling is expected to prevail; however, the special design of the pretreatment clarifier is expected to allow relatively complete settling of the iron-aluminum flocs; removal of this sludge will be aided by rake type agitator arms which act as a centrifuge to further concentrate the slurry in a bottom center well. Due to the rather non-compressible settling characteristics of the sludge, a very dilute underflow is expected ranging from 1 - 15 percent solids, depending on the effectiveness of the anti-flocculent and the rake arms. Therefore, dewatering of the sludge is very important in order to recover the valuable AMD, and also to hold to a minimum the cost of sludge disposal. Thus, the underflow slurry is pumped to a high speed disc-bowl centrifuge which will recover most of the AMD water, sending it back to the clarifier feed zone. The partially dewatered sludge containing up to 20-50 weight percent solids is then mechanically conveyed to disposal barrels or tank cars, from whence it will be either sealed in mines or deep-welled below the river bed. The centrifuge contains a manually adjustable batching nozzle and pulse control which will maximize the sludge dewatering operation.

Removal of Sulfates and Carbonates from AMD

Pretreated, neutralized mine drainage from the overflow weir of the pretreatment clarifier is pumped to the pressurized desulfating section of the production plant. The feed is distributed in parallel to four barium exchangers. Barium loaded ion exchange resin is hydraulically conveyed from the regeneration area to three resin screens in parallel, which in turn send the resin retains to each of the first three exchangers. The resin feed lines to the reactors are equipped with rotary vane feeders with preset timer control. Plant air is available to equalize reactor pressures in the resin feeders. Compressed flue gas from the Barium Conversion Area is supplied to the first exchanger at 75 psig. Each exchanger is equipped with relief and control systems, so that the pressure will be gradually let down until the last exchanger is operating at only 3 psig.

Thus, the CO_2 in solution will vary from 1750 ppm in the first, down to 440 ppm in last exchanger. The sulfate to carbonate ratio in the reactor chain is expected to approach unity to an extent which will allow just enough elution of barium from the resin to incur complete desulfating of the AMD. Thus, the parallel feed

arrangement and pressurized system are both seen as excellent means of monitoring the barium ion concentration in the AMD; this is important in both preventing the precipitation of barium sulfate in the resin beads and fostering its precipitation from the AMD.

Cascading from one barium exchanger to the next, the total flow leaves the last vessel, flowing by gravity to the primary screens where the resin is retained and the AMD, containing barium sulfate fines, is pumped to the degasifier column. The AMD enters the top or fifth tray of the "A" Section of the column; air is blown from the "A" Section bottom, contacting and freeing the dissolved CO_2. The AMD-sulfate containing barium then passes to the bottom or "B" Section of the column; concentrated sulfuric acid is metered to the top tray (20th) of this section and reacts with the carbonates which formed during the ion exchange cycle. CO_2 is evolved and is contacted with air from a blower. Thus, the degasified and decarbonated AMD leaves the bottom of the column and is pumped to the terminating reactor. The total CO_2 and air leaves the top of the "A" Section to atmosphere.

In the terminating reactor, AMD containing both precipitated and some dissolved barium is mixed with pretreated AMD containing sulfates which react with barium to form a precipitate. Both barium sulfate formation and crystal growth are fostered in the irreversible, and therefore terminating steps of the reaction model (see page 11).

The AMD - sulfate slurry is then gravity fed from the terminating reactor overflow weir to the thickener. Flocculent is introduced along with the slurry to the feed reaction zone of the clarifier, which promotes agglomeration of the fines. Clarified AMD, which is essentially free of sulfates and carbonates, overflows the weir and is collected in a surge tank for pumping to the product filter.

Underflow, consisting of 20 to 40 weight percent barium sulfate suspended in AMD, is pumped to a centrifuge where it is dewatered, resulting in a cake containing 20 to 50 percent water, which is conveyed to the barium conversion area.

The sulfate clarifier overflow may contain up to 100 - 200 ppm turbidity as barium sulfate fines. This shall be removed in a product filter system containing precoated cartridges in a continuous cycle. The filter is equipped for alternating back-washing-precoating, and on-line operations.

Pretreated, desulfated, decarbonated and filtered product AMD emerges from the filter.

Resin Regeneration

The ion exchange resin that was separated by screening from the desulfated AMD containing barium sulfate fines, in the primary filter, is partially exhausted, consisting of sodium, calcium, magnesium, and mostly of barium ions. The resin falls from the screen into an agitated ion exchanger where a 0.1N sodium chloride solution is introduced. Due to an excess of sodium chloride present in the system and with equilibrium conditions prevailing, some barium will be eluted from the partially exhausted resin. However, because of the selectivity of the resin toward barium, it is expected that most of the calcium and magnesium will be eluted rather than the barium. Also, a small amount of the desulfated AMD, containing unreacted barium, from the degasifier feed pump may be introduced to prevent barium elution by the salt. The resin-salt solution slurry overflows the exchanger weir into a secondary screen which passes the waste stream, while retaining the resin; the latter is transferred by bucket elevator to the resin loading section. Resin is passed to one of two moving bed loading columns. Each column consists of internal fiberglass tube bundles and distributors to prevent bridging and plugging of the resin beds. The resin falls by gravity counter-current to ascending barium containing liquor.

The barium loaded resin is collected in the bottom sections of the loading columns. The streams are then combined and flow into the rinsing column which also consists of an internal fiberglass tube bundle with distribution and collection system. The resin falls by gravity in counter-current flow to the ascending process water which removes any entrained regenerant from the resin pores. Rinsed, barium loaded resin leaves the bottom of the rinse column and is passed through the suction of an eductor and is hydraulically conveyed by 100 psi process water to the resin feeding system screens in the desulfating section.

The regenerant solution is produced in the barium conversion area and is sent first to a feed tank where it is diluted with process and rinse water to the proper barium concentration (0.1N) from whence it is pumped to the parallel loading columns.

Effluent Treating

The effluent from the top (clarification) sections of the loading columns consists mainly of dissolved sulfides and hydrosulfides of sodium with traces of barium, calcium, and magnesium ions. The solution flows by gravity, into an agitated treating tank where some pretreated AMD is also introduced. The sulfate in the AMD reacts with the traces of dissolved barium to form an insoluble precipitate. The slurry is pumped to a separator in the carbonation area where the precipitate is removed by gravity settling; the clear effluent overflows the weir and is pumped to the carbonation column. The barium sulfate pulp is drained from the separator bottom and is pumped to a centrifuge which dewaters the slurry generally from 50 to 80 percent solids. The cake discharge is then conveyed to the barium conversion section, the liquid filtrate being returned to the separator or transfer pump suction line.

Waste Treatment

The waste stream from the secondary resin screen in the resin purification area of the regeneration section contains mainly a dilute solution of sodium, calcium, and magnesium chlorides, with traces of barium. In order to remove barium in the form of sulfate, the waste stream flows by gravity into an agitated tank where it is mixed with pretreated AMD containing dissolved sulfate. The waste stream containing barium sulfate fines is passed into a waste separator which removes a clear, barium free waste stream as overflow to drain, and a barium sulfate slurry as underflow, which is returned to the sulfate centrifuge for dewatering.

Barium Sulfate Conversion

Pulverized coal is received in hopper bottom cars and is unloaded and conveyed to conical bottom storage bins. Pulverized barites are also received and stored for barium makeup. The coal is conveyed from storage to a feed hopper, while barium sulfate slurry is simultaneously conveyed from the sulfate centrifuge and the sulfate recycle centrifuge (unreacted sulfate from the leaching operation) to another feed hopper where barite makeup is also added. Both bins are equipped with vibrators, feeders, and controls necessary to maintain a preset, ratio of coal to sulfate into a geared mixer which blends the two constituents. The mixture is then hoisted to a mixed sulfate surge bin which feeds the roasting system.

Initially, the net barium sulfate-carbon mixture is dried to 5 - 10 percent moisture in a direct heat rotary dryer which uses hot flue gas from the calciner in counter-current flow as a drying medium (an auxiliary burner is also provided). The relatively dry mixture is then fed to a rotary drum pelletizer. The barium sulfate, which has a particle size averaging one micron, and the pulverized coal, passing through a 100 mesh screen, are balled to pellets or modules by the rotating action of the pelletizer surface.

The pellets enter the calciner which is a direct heat, brick-lined rotary kiln, fired with natural gas in counter-current flow; controls at the firing end maintain a reducing atmosphere. The intimately mixed coal reacts with the barium sulfate at a temperature of about 2000°F to produce barium sulfide at a conversion rate of 92 percent. Because the barium sulfide is highly reactive at elevated temperatures and is rapidly oxidized to the sulfate form in the presence of oxygen (air), the calcine must be cooled below 200°F before grinding. Cooling is effected in an indirect water spray rotary cooler which utilizes process water at 77°F.

The hot flue gases from the kiln are passed through the rotary dryer, where they are cooled below 200°F and contain approximately 20 percent (vol.) carbon dioxide. Part of this is blown to the carbonation section of the plant to be described later. The other portion of the flue gas is compressed to 100 psig and is sent to the pressurized exchangers in the desulfating section. Cyclones are included with both the calciner and dryer to eliminate entrainment in the flue gas.

The cooled pellets are then conveyed to a calcine mill which grinds the pellets, which consist of approximately 88 percent barium sulfide, 10.5 percent barium sulfate and 1.5 percent ash, to about 20 microns fineness at 176°F. The mill includes equipment for classification and dust collection.

The calcine fines are conveyed to a surge bin which feeds into the first reactor of two in series, which are part of a two-stage counter-current leaching operation. Process water is preheated in the calcine cooler and combined with heated wash water from the sulfate recycle centrifuge. This combined stream is then passed

into the Second Stage Contactor which dissolves any entrained sulfides which are in the First Stage Thickener underflow. The slurry then overflows into the Second Stage Thickener which separates the undissolved sulfate and ash by gravity settling; the underflow is pumped to the sulfate recycle centrifuge which dewaters the sulfate. Approximately a 50 - 70 percent (by wt.) discharge cake is conveyed, along with the barium sulfate from the dewatering section of the desulfating process, back to the feed hopper for mixing with coal. The filtrate is combined with the feed to the Second Stage Contactor. The Second Stage Thickener overflow, consisting of a dilute barium liquor, is then heated from 118 to 156°F and is passed into the First Stage Primary Contactor where it is mixed with the calcined fines from the mill section; the latter is fed at a preset ratio to the amount of process water which is fed to the Second Stage Contactor. The partially dissolved slurry overflows into the First Stage Secondary Contactor, where most of the remaining barium sulfide is dissolved. The slurry, consisting of barium sulfate, ash, and some undissolved sulfide entrainment, with the sulfide solution is gravity fed to the First Stage Thickener. The sulfate, ash and entrained sulfide settles out and the underflow is pumped to the Second Stage Contactor where the remaining traces of sulfide is dissolved in the first stage feedwater. The full miscella (barium containing liquor) from the First Stage Thickener overflow is pumped to the Feed Dilution Tank in the resin regeneration area.

Following centrifugation and washing, part of the sludge from the recycle centrifuge is discarded (blowdown line) to keep down the ash concentration.

Carbonation

The treated effluent from the loading columns in the Resin Regeneration section is pumped to a separator which pumps the barium sulfate underflow to a centrifuge for dewatering. The separator overflow, consisting of less than 0.1N sodium sulfide with trace barium, is pumped to the Carbonation Column in which it flows by gravity from the top stage (tenth) to the bottom section in which flue gas is fed counter-currently. Each stage consists of a sieve tray arrangement with a paddle-type agitator. The flue gas is blown from the roasting section of the barium conversion loop and contains 20 percent (by vol.) CO_2. The carbon dioxide contacts the sodium salt solution

and reacts to form sodium bicarbonate. Hydrogen sulfide is formed during the reaction and is passed out the top along with the flue gas. This is blown to the sulfur recovery plant which converts the H_2S to elemental sulfur which is stored and sold as a by-product. The sodium bicarbonate solution is returned to the pretreatment section where it is used in the neutralization of AMD. Any excess of sodium bicarbonate will be discarded.

Sulfur Recovery

The sulfur recovery plant will be purchased as a package unit and will recover 1.013 tons/day of sulfur (elemental). Flue gas containing from 10-20 w/o hydrogen sulfide will be supplied to the plant at a rate of 100-150 CFM.

Recovery of Salable By-Products and Logistics

By-Product Recovery

Four by-products could, in theory, be produced in the operation of the AMD Neutradesulfating Production Plant:

1. Sodium bicarbonate solution (0.7 percent by wt.) can be produced in excess over that needed for pretreatment. This would yield about 2 - 2.5 tons/day solids. However, the cost of recovery and purification of this product is prohibitive for yields in this range.

2. Sludge from the pretreatment area, consisting of iron oxides, aluminum hydroxides, hydrates of both, and calcium carbonates, could be dried to yield 1.6 ton/day. However, to date there is no market value for such a mixture, and separation techniques could not be justified from both an operational and economic basis.

3. Sulfur will be recovered by a packaged process which converts H_2S in flue gas into elemental sulfur at a rate of 1.01 ton/day, which is essentially pure and has market value.

4. A waste stream from the sodium completion step of the resin regeneration section, which has been treated to remove any dissolved barium, overflows from the waste treatment clarifier into a drain. It consists of dilute (1%) quantities of sodium, calcium and magnesium chlorides. Cost of separating and recovering of individual components are prohibitive and impractical. The stream, as is, has no known market value or use.

Logistics Associated with the Neutradesulfating Process

In a 1MM GPD neutradesulfating production plant, the relatively low rates of by-product accumulation and chemical consumption require only one railroad car per two weeks which would carry all the chemicals necessary to maintain a full production rate for that period. Sulfur being the only marketable by-product will need but one car every three months.

Therefore, trucking the materials seems to be a practical alternative. A typical self-unloading pneumatic bulk trailer will carry 15 - 20 tons of sulfur. Ordinary dump trucks with tight-fitting tarpaulin covers could also be used if the sulfur is bagged. Only one truck is needed per two-week period for the by-product; whereas three trucks per two-week period would be required for the entering chemicals. Catalytic's design has provided for two-week storage capacity.

An initial supply of process water is required for startup, which shall be produced thereafter by the process. Therefore, a 20,000 gallon storage pond for process water requirements has been included (10' x 20' x 2'). Also, an initial 1,000 cubic feet of resin will be required.

Table XVII describes the trucking (or R.R.) traffic for the plant. Table XVIII lists utilities for the production plant.

TABLE XVII

Production Plant Daily Traffic Schedule

	Production Rate of Usage		Transportation By R.R. or By Truck		
	Tons/Day	Tons/Car	# Cars	Ton Truck	# Truck
1. Products (leaving)					
Sulfur	1.013	50 - 70	1/3 Mo.	15 - 20	1/2 Wk.
Sludge(*)	1.608	- deep-welled -			
Waste Stream(**)	3.26	- discarded -			
2. Chemicals (entering)					
Coal	0.9	50 - 100	-	20 - 30	1/2 Wk.
Salt Cake	3.636	70 - 100	1/2 Wk.	30 - 40	2/2 Wk.
Barites	0.12	150 - 180	-	60 - 80	1/Yr.
Sulfuric Acid (42 gal. bbl.)	0.3	60 - 120	-	25 - 35	1/3 Mo.
Flocculent	0.084	35 - 70	-	15 - 20	1/6 Mo.
Resin	0.534 (per yr.)	60 - 70	-	-	-
	4.742 Ton/Day	70 - 100	1 car/2 Wk		3 Truck/2 Wk.

(*) Dry Basis - Sludge to be welled as 50% water slurry.
(**) Dry Basis - Exits in a 0.5% solution by weight.

TABLE XVIII

Production Plant

Utilities Summary

	Flow	Condition
Steam	100 Lbs/hr.	@ 5 psi Sat'd.
Process Water	240 GPM(*)	25 psig
Cooling Water	50 GPM	25 psig
Electricity	850 KW	
Plant Air	100 SCFM	@ 80 psi

(*) Total process water input.

PLANT EQUIPMENT

The production plant is a conceptualized design for a 1MM GPD commercial unit. All sizes are shown on the Appendix D drawings R-211 and R-212, which include production and waste recovery sections, respectively. Cost estimate for a 1MM GPD unit was based on the prices of equipment shown on these drawings and described as follows:

Furnace

A natural gas fired packaged boiler producing saturated steam at 20 psig with a capacity of 100,000 BTU/hr. shall be furnished.

Reactors

All reactors shall be tar modified epoxy-coated or rubber-lined carbon steel vessels, having ASME dished heads, and top entering, center mounted, variable speed, turbine-type, rubber-coated steel agitators.

Towers

External tar modified epoxy-coated carbon steel with fiberglass distribution system and internals are specified for the moving bed Resin Regeneration and Rinsing Columns.

The Degasifier Column is divided into two sections; the top section has a 5-stage sieve tray, 1-pass arrangement and the bottom section has 20 stages with a 2-pass, sieve tray design. Each has an air distributor system.

The Carbonation Column is 10 stages with a turbine paddle agitator on each perforated tray, running from a central shaft. These towers are of epoxy-coated carbon steel.

Heat Exchangers

One rotating solids cooler and two conventional shell and tube heaters are of carbon steel construction.

Vessels

In general, 316 stainless steel or polypropylene are specified for chemical service, rubber-lined or epoxy-coated carbon steel for acid service, epoxy-reinforced fiberglass, or teflon lining, for resin conveying and feed tanks, and carbon steel for storage. Exceptions include monel, and high silicon iron for special chemical and waste applications.

Pumps

Centrifugal pumps are specified for AMD and most chemical services, and are generally of stainless steel with wetted parts. Metering pumps for special chemical feed systems have stainless steel wetted parts. Diaphragm pumps are specified for many of the solids handling applications and are hypalon lined, with hypalon diaphragm and quick opening valves.

Materials Handling

Sludge, sulfate, and coal conveyors are either the belt, flight, or tubular type. Rubber belts with moulded rubber cleats, dust-free totally enclosed drag flights, and carbon steel with stainless steel links and neoprene flight material shall be used. Coal storage bins and conveyor feed lines shall include flanged discharge openings, terminals, anti-friction head bearings, take-ups, and drip-type lubricating systems.

Sulfate and carbon feeders shall be of carbon steel and are complete with vibrating mechanism and supports.

A 40-foot bucket elevator with lexan buckets, plexiglass inspection windows, and mild steel housing with acid resistant coating shall be used for resin service; and an inclined 43-foot vertical, 5-foot horizontal travel skip hoist elevator of epoxy-coated carbon steel shall be used for calcination feed.

A 20-foot vertical, 5-foot horizontal inclined bucket elevator of epoxy-coated carbon steel shall be used for the leaching feed system.

A hydraulic conveying system, which includes teflon coated lines, and PVC eductor are used to transfer resin feed.

The Sulfate-Carbon Mixer consists of dual, stainless steel agitator paddles with a retention and dam at discharge end and epoxy-coated steel trough.

The Sulfate-Carbon Dryer is a counterflow rotary self-supported drum with auxiliary steam heating coil, and is of epoxy-coated steel construction.

The Pelletizer shall be a rotary-coated carbon steel unit with stainless steel interior surface.

The Calciner shall be a natural gas-fired rotary kiln of brick-lined carbon steel, equipped with inlet and outlet feed, natural gas, air, and flue rotary connections.

The Calcine Mill is a comminuting machine with 316 stainless steel chamber and 414 or 420 hardened, tempered stainless steel hammer blades, with stainless screens. This unit also includes a stainless steel collector and cyclone, cast iron vacuum producer, and a negative pressure rotary air lock.

All of the above mentioned equipment are for continuous service, and includes epoxy-coated or acid-resistant painted surfaces.

Filters, Screens, Centrifuges, and Other Separators

Clarifiers shall be field erected and are complete with central inlet feed chambers, rakes, motorized driver, controls, alarms, walkways, etc. All wetted parts are to be tar-modified epoxy-coated carbon steel. The clarifiers generally include counterflow detention hoods, orifice holes, and collection flumes for optimum clarity effluents; also, Neptune 60^{o} inclined tube modules are provided to increase collection capacity.

The Product Water Filter shall consist of two carbon steel units each containing 260 disposable cartridges, of polypropylene media and matrex on 304 stainless steel cores, with a 1 micron rating. One unit shall be backwashed and precoated while the other is in service. Pressure drop measuring devices and manually operated valves are included.

Vibrating screens are used to separate resin from various slurry streams. All units will be furnished with plastic-coated vibration eliminator springs, epoxy-coated externals, 316 stainless steel wetted parts, and neoprene connectors on discharge spouts. All are single stage except the Exhausted Resin Secondary Screen which has an additional deck for removal of attrited resin beads.

The Traveling Water Screen consists of a belt of inclined screening panels with clear opening stainless steel wire mesh, and bottom ledgers to retain floating and suspended matter. Jet sprays backwash the material into a trough or disposal sluice.

The centrifuges are continuous horizontal model decanters of various horsepowers and bowl sizes, equipped with motor, starter, and vibration isolators. The exception is the sludge centrifuge which contains a continuous vertically wheeling basket from which the sludge will be periodically skimmed by timer control and is equipped with spring mount and flexible connections. All units shall be of 316 stainless steel wetted parts and epoxy or chemically coated externals.

Agitators

Generally, top entering, center-mounted units of rubber-covered or epoxy-coated carbon steel will be used. Reactor units will have dual turbine blades with stuffing boxes, 8-inch flanges for top center mounting, and stabilizing rings.

Smaller units with less vigorous mixing requirements and open tank operations shall be portable propeller type. Chemical dissolution service will use stainless steel units with high powered center-mounted propeller blades.

Packaged Units

The Instrument Air Compressor consists of a centrifugal drive to deliver oil free air at 100 psig, a vertical air receiver, and air dryer. The Flue Gas Compressor is of similar design but includes an aftercooler and a special bronze pump and trim.

Centrifugal blowers will be used for supplying air to degasifier and kiln, and shall be of tar-modified epoxy-coated carbon steel. A stainless steel blower will be used to transfer H_2S containing flue gas to the Recovery Section.

A Salt Lixator, consisting of a concrete cubicle divided into two sections, supplies a concentrated brine solution to the process. Rock salt is dumped in the loading hatch of either cubicle in which a water level is maintained. The solution is collected in a brine well for pumping. Each cubicle can be drained and cleaned independently.

LAYOUT

A conceptualized plan for a 1MM GPD commercial unit is sketched in dwg. B-211 Appendix D. This includes estimated sizes for offsite considerations, and includes two-week storage allowances for incoming chemicals. Included are warehouse, maintenance, operating, and administration spacing considerations. Also, a 20,000 gal. pond is included for storage of process water for startup requirements. Equipment is grouped in block form and attention is given to both accessability and proximity, which at the same time, attempts to hold materials handling costs to a minimum.

The sketch assumes that this location relative to the river side is possible; it is also assumed that railroad and roadway routings could be oriented in the illustrated fashion. However, there is a built-in flexibility in the blocked plan that would allow for easy manipulation of all vital units. The sulfur recovery plant space is an estimate due to lack of available sizing data for the packaged unit in this relatively low capacity range.

Approximate overall dimensions of the land required for layout of the 1MM GPD unit are 350' x 200', or 1.6 acres.

ECONOMICS

Capital Investment

The estimate for the capital investment of the neutradesulfating plant and by-products facilities is based on vendors' written or verbal quotations for the major equipment. The neutradesulfating plant has been regarded as an independent "grass roots" plant including storage warehouses, offices, laboratory, etc. A 14-day storage capacity for chemicals and by-products is included.

The total capital investment for the 1MM GPD plant of $4,956,600 is based on a major equipment cost of $1,563,200 and was built up to include all construction cost including a 15% contingency and a working capital of 10%. No charges were made for land. Based on this, the total capital investment for 10, 25, and 100MM GPD were calculated at a prorating factor of six-tenths. A summary of investment capital is presented in Table XIX.

Operating Costs

The operating costs were calculated for an operating year of 328 days and are presented below on both a unit cost basis and an overall annual basis as shown in Table XX, for a 1MM GPD plant. The basis for the various charges follows.

Direct Costs

Chemicals:

Barite makeup is taken at $30/ton. Its consumption is dependent on the efficiency of the sulfate clarification. The loss due to entrainment in the overflow is estimated as 1.5% of the barium sulfate formed in the desulfating ion exchange cycle or approximately 10 lbs/hr.

Coal is used in the reduction of barite in the rotary kiln (calcination step) at a rate of 75 lbs/hr. The coal is taken at a cost of $10/ton for powdered anthracite at the plant site.

Salt (NaCl) is used to transfer the spent resin into solely the sodium form. A rate of 300 lbs/hr. is needed. The price is taken at $12/ton.

TABLE XIX

CAPITAL INVESTMENT FOR NEUTRADESULFATING PLANTS

1MM GPD PLANT		
Purchased Equipment	$1,563,200	
Fixed Capital Cost		$4,506,000
Working Capital		450,600
Total Capital Investment		$4,956,600
10MM GPD PLANT		
Purchased Equipment	$6,200,000	
Fixed Capital Cost		$17,900,000
Working Capital		1,790,000
Total Capital Investment		$19,690,000
25MM GPD PLANT		
Purchased Equipment	$10,770,000	
Fixed Capital Cost		$31,100,000
Working Capital		3,110,000
Total Capital Investment		$34,210,000
100MM GPD PLANT		
Purchased Equipment	$24,700,000	
Fixed Capital Cost		$71,200,000
Working Capital		7,120,000
Total Capital Investment		$78,320,000

TABLE XX

ECONOMIC EVALUATION FOR A 1MM GPD
NEUTRADESULFATING PLANT

TREATING COSTS		$/1000 Gallon		$/Year	
DIRECT COSTS					
Chemicals					
Barites	@ $30/ton	.002		656.	
Coal	@ $10/ton	.009		2952.	
Salt	@ $12/ton	.044		14432.	
Flocculent	@ $.73/lb.	.012		3936.	
Resin	@ $17/CF.	.0002		66.	
Sulfuric Acid	@ $27/ton	.008		2624.	
Subtotal Chemical		.0752		24660.	
Utilities					
Steam Self-Supporting					
Process Water	@ $.22/1000GAL.	.074		24272.	
Electricity	@ .0075/KWH	.147		48216.	
Fuel Gas	@ $.35/MM Btu	.008		2624.	
Subtotal Utilities		.229		75112.	
Labor & Supervision					
Direct Labor		.220		72160.	
Supervision		.044		14432.	
Maintenance		.040		13120.	
Subtotal Labor		.304		99712.	
Repair and Maintenance		.386		126608.	
Supplies (15% of Maintenance)		.058		19024.	
Total Direct Cost			1.052		345122.
INDIRECT COSTS					
Plant Overhead (50% prod. labor)		.152		49856.	
Payroll Overhead (20% prod. labor)		.061		20008.	
Packing and Shipping (*)		.097		31816.	
Total Indirect Cost			0.310		101680.

(*) Includes waste transport allowance for sludge

TABLE XX

TREATING COSTS	$/1000 Gallon		$/Year	
FIXED COSTS				
Depreciation (4.6%, 30 yrs.)	.943		309304.	
Property Tax (2% Fixed Cap./yr.)	.275		90200.	
Insurance (1% Fixed Cap./hr.)	.140		45920.	
Total Fixed Cost		1.358		445424.
Total Treating Cost		2.720		892226.
CREDITS				
By-Product Sulfur @$30/ton	.030			
Total Credits		.030		9840.
Net Unit Cost of Neutradesulfated Water		2.690		882386.

Flocculent is used to improve settling rates in the pretreatment and sulfate clarifiers. A rate of 0.7 lbs/hr. is needed (*), but due to the high price of $.73/lb., the relative cost is significant.

Ion Exchange Resin makeup rates of .012 CF/day are accounted at a nominal cost of $17/cubic foot.

Sulfuric Acid is used in the bottom section of the degasifier column to remove remaining carbonates and bicarbonates formed in the pressurized desulfating unit, which cannot be removed by merely air sparging. This amounts to 1.6 gph, at a unit cost of $27/ton of 66° Be Acid.

Utilities:

Electricity is the main contribution to the utility costs, being consumed at a rate of 825 KWH. The recommended price of $.0075/KWH is used.

Fuel Gas is a minor cost, and is taken at $.35/MM BTU. 1MM BTU/hr. is required for the preheat and calcination of barium sulfate.

Process water consumption is due to loss of water in outgoing waste streams amounting to 83 GPM; water cost is taken as $.22/1000 gal.

Labor and Supervision:

A total of eight operators ($9,000/yr.) is needed for a 7 day, 40 hour, 3 shift/day, production week. One supervisor ($14,000/yr.), two maintenance men ($6,500/yr.) and two lab technicians ($8,000/yr.) are on a 40 hour week; administration includes a plant director ($15,000/yr.), technical advisor ($12,000/yr.), and a secretary ($6,500/yr.) all of whom are salaried. Total labor and supervision comes to 11.4% of manufacturing cost.

(*) Based on 1 lb/ton dry solids

Repair and Maintenance Charges were estimated from average maintenance costs of similar equipment from past applications. These were updated using a maintenance index. This amounts to 2.81% of fixed capital cost. Labor due to special maintenance problems is a part of this charge (usually about 50% of repairs including 10% supervisory labor).

Supplies are estimated as 15% of maintenance and repairs.

Indirect Costs:

Plant overhead is taken as 50% of the productive labor cost, with a 20% of productive labor allowance for payroll overhead. Productive labor includes direct labor, supervision, and maintenance.

Packing and shipping charges are taken as $1.00/ton for sulfur, and .03¢/lb. trucking allowance is made for waste (sludge) disposal.

Fixed Charges:

Depreciation charges are amortized at 4.6% for 30-year expected life.

Property Tax and Insurance are taken at 2% and 1% of fixed capital investment per year respectively.

By-Product Sale

Sulfur is the only by-product that will be upgraded for sale. All the barium sulfate produced is used in the conversion and regeneration steps.

a. The pretreatment sludge and the waste stream have no realizable market value at the present time.

b. Though the neutradesulfating process does generate other materials with a soluble potential, sulfur is the only one that has to be treated in one way or another to reduce its strong polluting effect. At the same time, the reduction of hydrogen sulfide to sulfur is a well established process that will require an investment lower than that required by any treating system.

The 1MM CPD plant will produce close to one ton of sulfur per day that is rated at $30/ton.

Cost of Neutradesulfating AMD

The net unit treating cost sums up to $2.69 per thousand gals. of feed. This is equally correct with regard to 1000 gal. of treated water since an amount of water almost equal to the total purchased process water (added to product stream) leaves in subsequent waste streams.

Expansion of Cost of Neutradesulfating for Larger Capacity Plants

Contrary to the economic factors which were designated in the ground rules for the proposal (7), as stated in the introduction, the true expected life of equipment is more likely to fall in the 10-20 year range. Therefore, in Figure 23 the unit cost of neutradesulfating is shown as a function of plant capacity for 10, 20, and 30 year expected life spans. These costs are relatively high for capacities in the 1MM GPD range, but no significant change is noticed beyond the 25 MM GPD capacity. Figure 24 shows the effect of investment on the unit cost for 15 and 30 year lives. These figures are based on the simplified equation:

$$MC = 0.45 + (.0773 + 1.37\ crf\ (4.6-n) \times \frac{UFC}{S^{0.4}}$$

MC = Manufacturing Cost in $/1000 Gal.

crf = Capital Recovery Factor for 4.6% Interest over n years of life (Amortization)

UFC = Unit Fixed Capital investment for 1MM GPD plant in $/1000 gal/yr.

S = Plant capacity in MM GPD.

n = Expected life, years.

The assumptions are those stated in the Operating Cost Section; total labor and supervision was taken as 11.4% of manufacturing cost, and repair and maintenance is assumed to be 2.8% of fixed capital per year. These figures were calculated from the 1MM GPD treating costs from Table XX. A 10% allowance is made for working capital

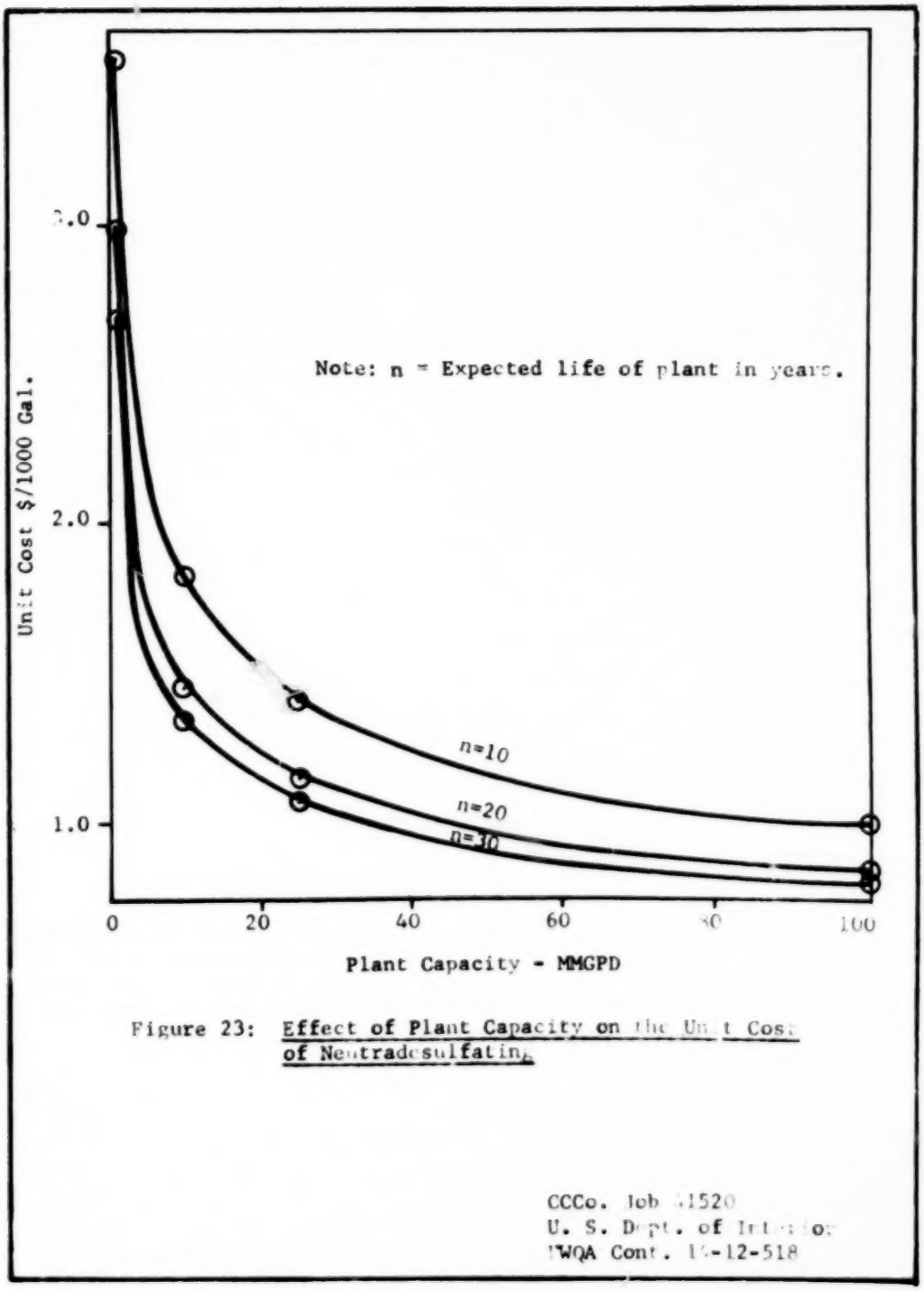

Figure 23: Effect of Plant Capacity on the Unit Cost of Neutradesulfatin.

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The curves of Figure 23 show that the cost for a 1MM GPD plant is relatively high, falling sharply as the plant capacity increases to 10MM GPD, then sloping off until no significant change occurs beyond the 25MM GPD capacity.

From Figure 24, it is noticed that capital investment has a great effect on the unit cost of a 1MM GPD plant, but has a much decreased effect on the 10 and 25MM GPD units. If capital investment were only 50% of that realized, the cost would be about $0.80/1000 gal. for a 10MM GPD plant with either 15 or 30 year lives.

However, if a 1MM GPD plant could be built for only half the estimated capital investment, the manufacturing cost would still be a relatively high $1.82/1000 gal. for a 15 year life, and $1.57/1000 gal. if a 30 year life were realized.

It can be seen from both figures that for the estimated base capital ($4,506,000), the 25MM GPD plant would be a good cut point with only a small saving realized after this point for additional capacity.

Economic Feasibility of Neutradesulfating Plant

Unless fixed capital could be sharply reduced,(*) the 1MM GPD plant would operate at a cost which is three times higher than some of the processes which have been reported (8). However, consideration should be given to a plant in the 10-25MM GPD range for which the economics are more favorable.

Future research developments and waste product marketability could shed new light on the subject. However, at the present time, the neutradesulfating of acid mine drainage waters would dictate the use of 10-25MM GPD plants at unit costs which would not likely be below $1.00/1000 gal. for a 30 year write-off.

(*) See page ix for new approaches to basic process, which offer potentially lower treatment costs.

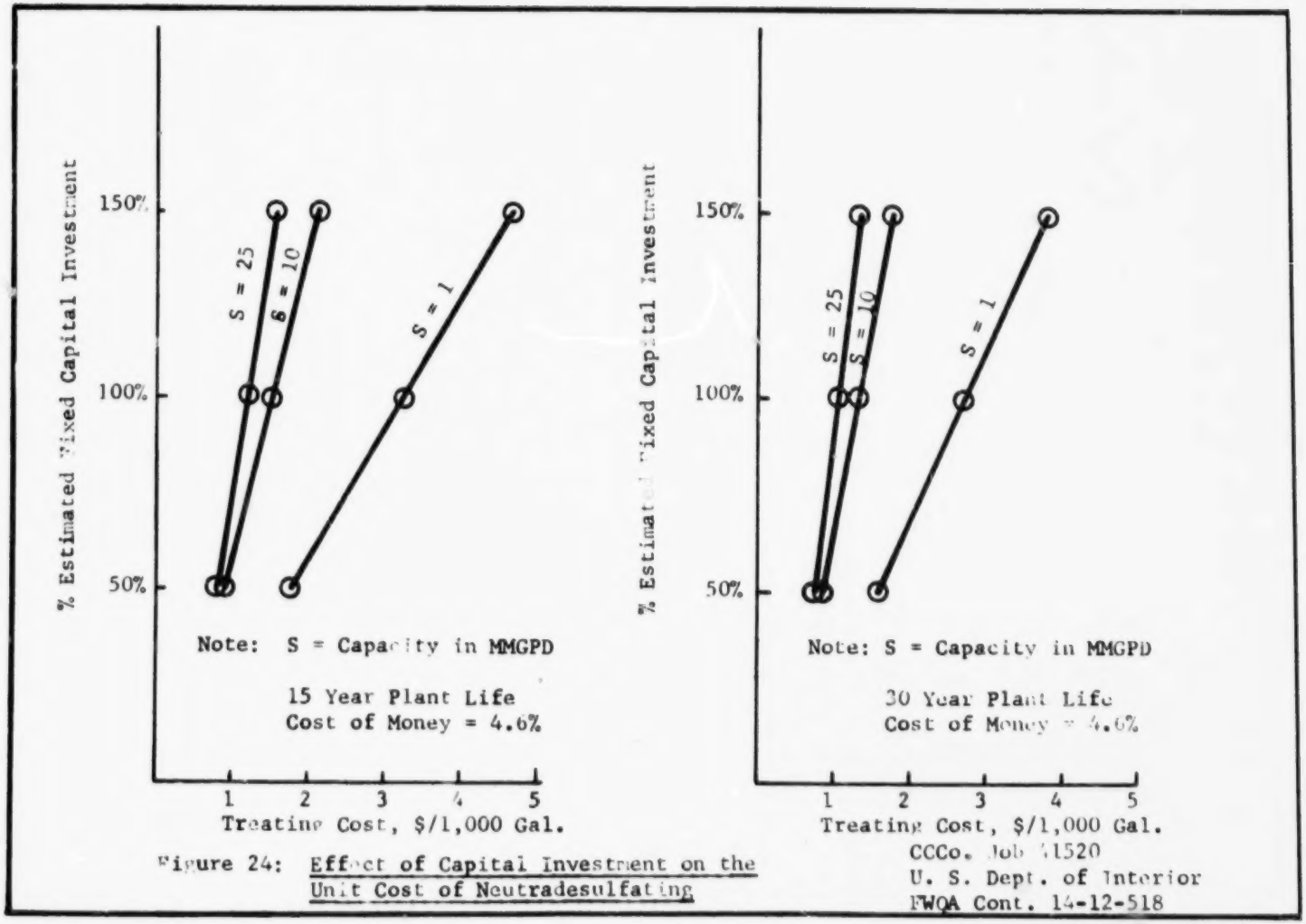
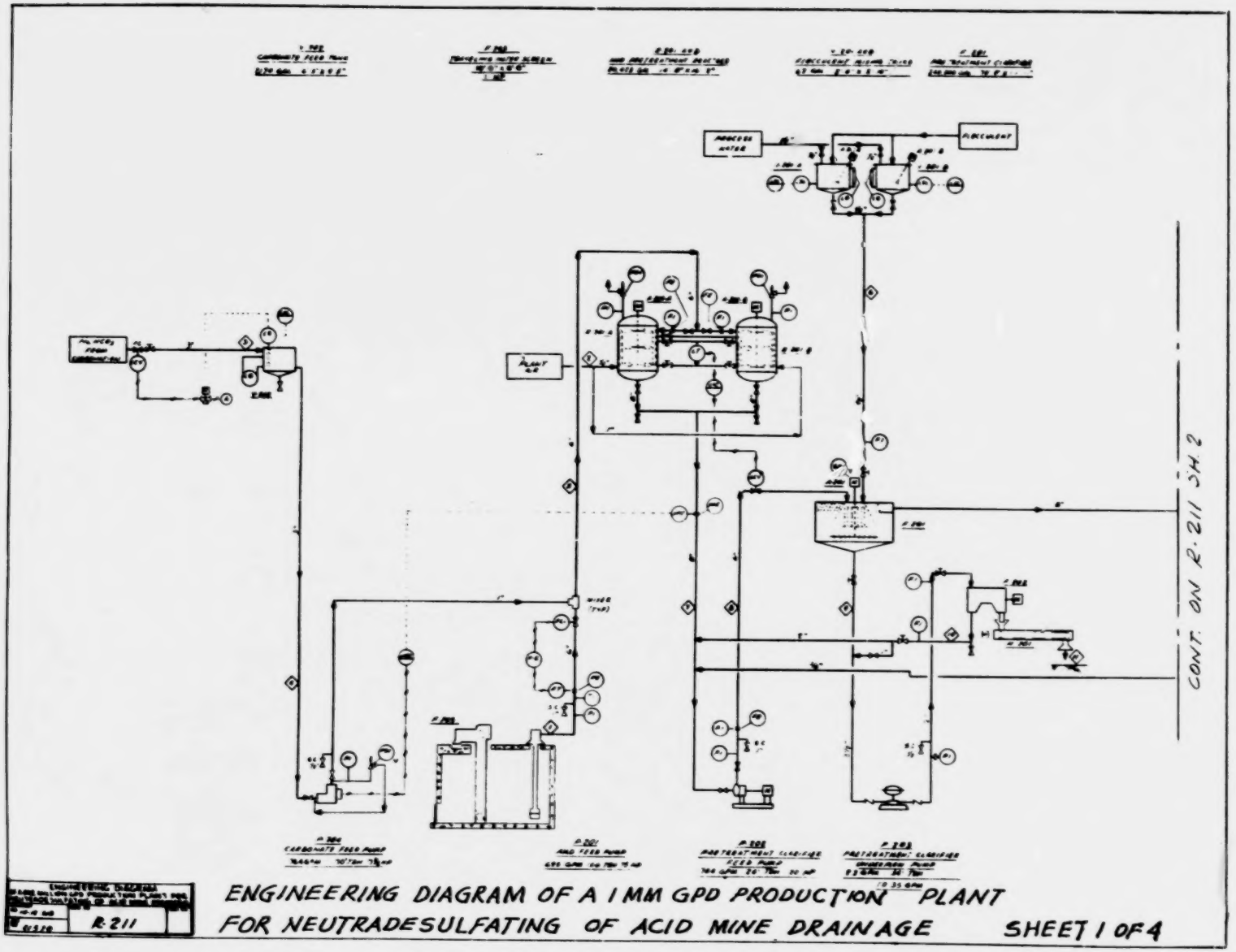
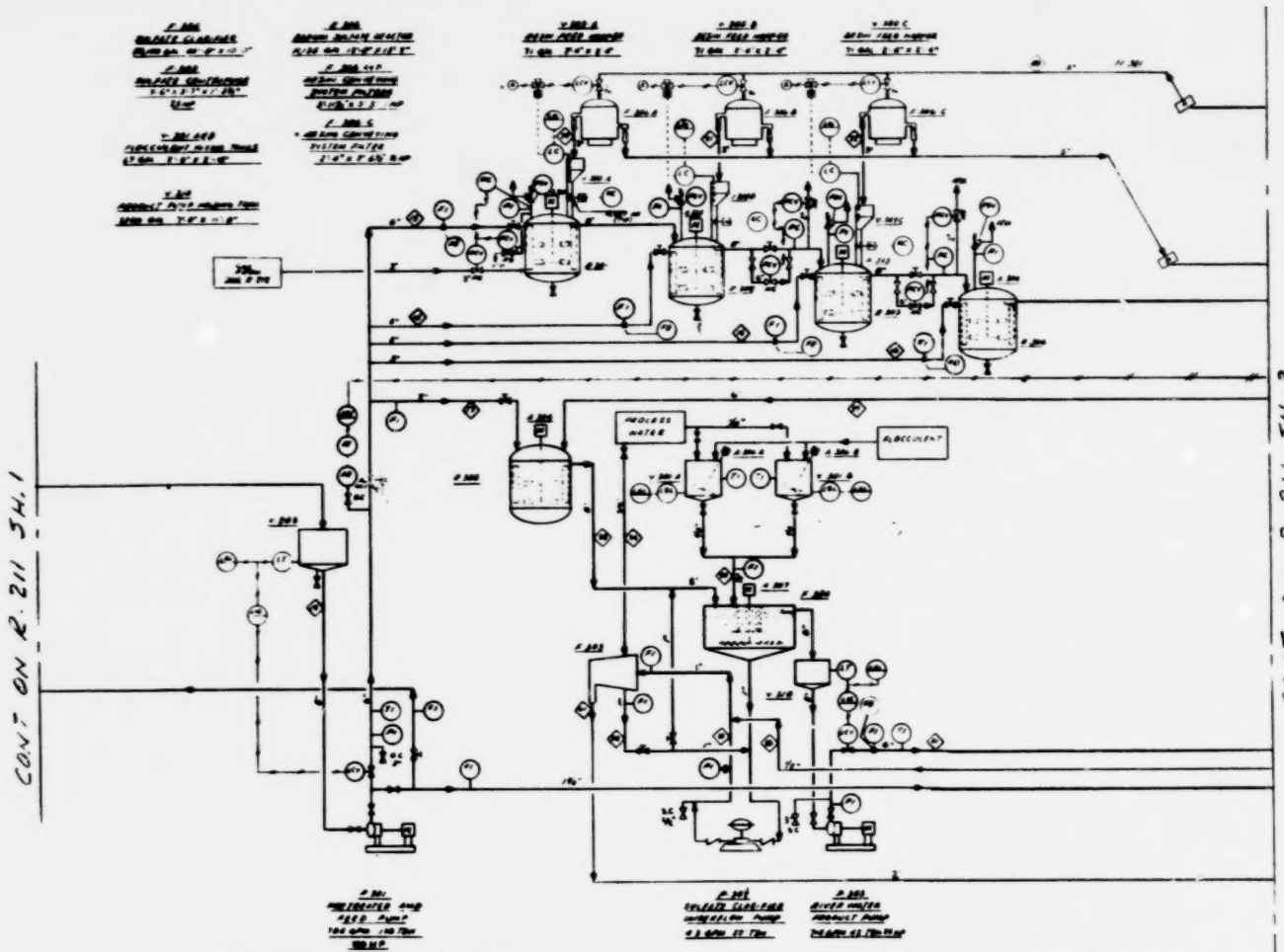


Figure 24: Effect of Capital Investment on the Unit Cost of Neutradesulfating

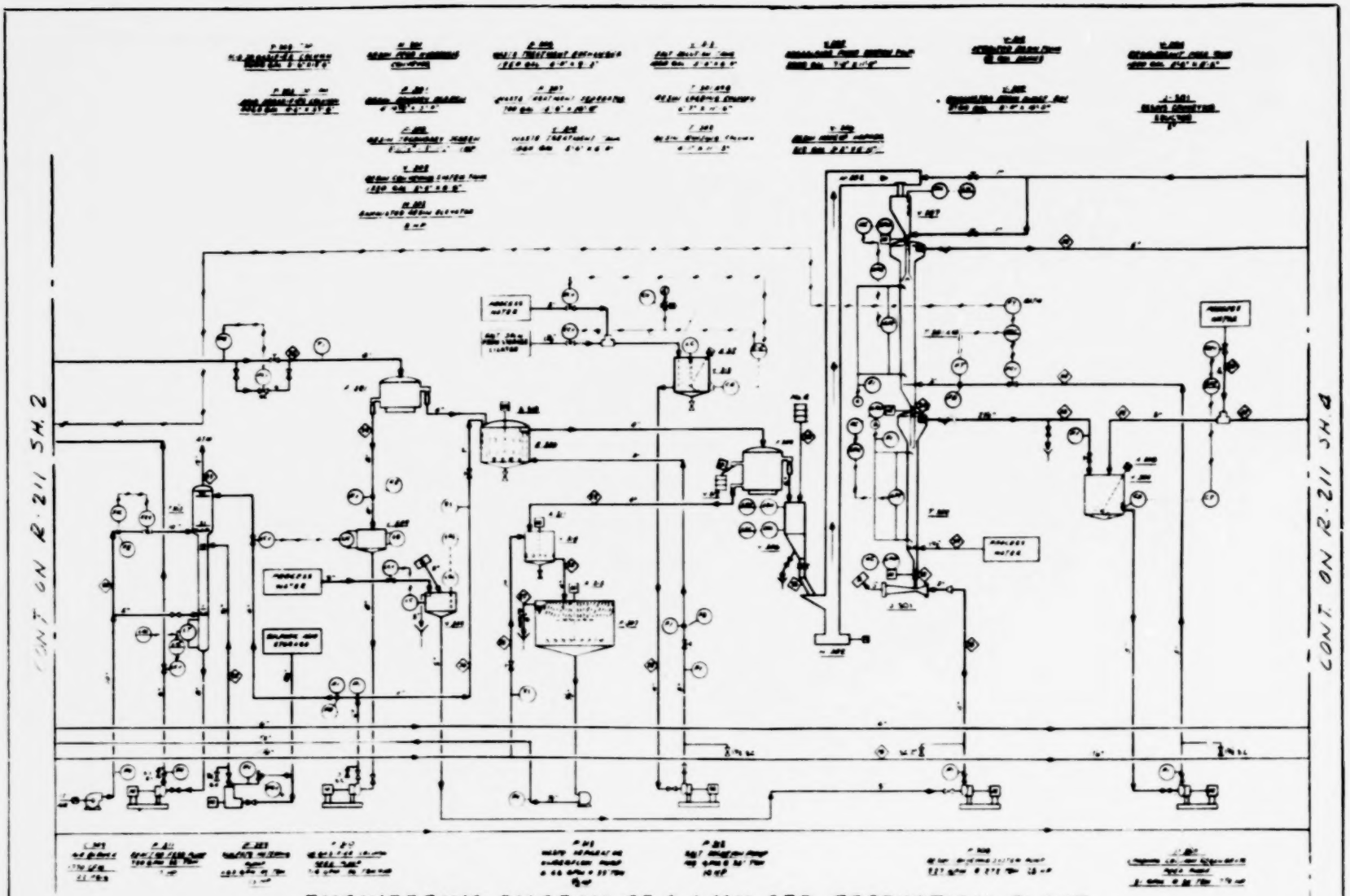


ENGINEERING DIAGRAM OF A 1MM GPD PRODUCTION PLANT
FOR NEUTRADESULFATING OF ACID MINE DRAINAGE SHEET 1 OF 4

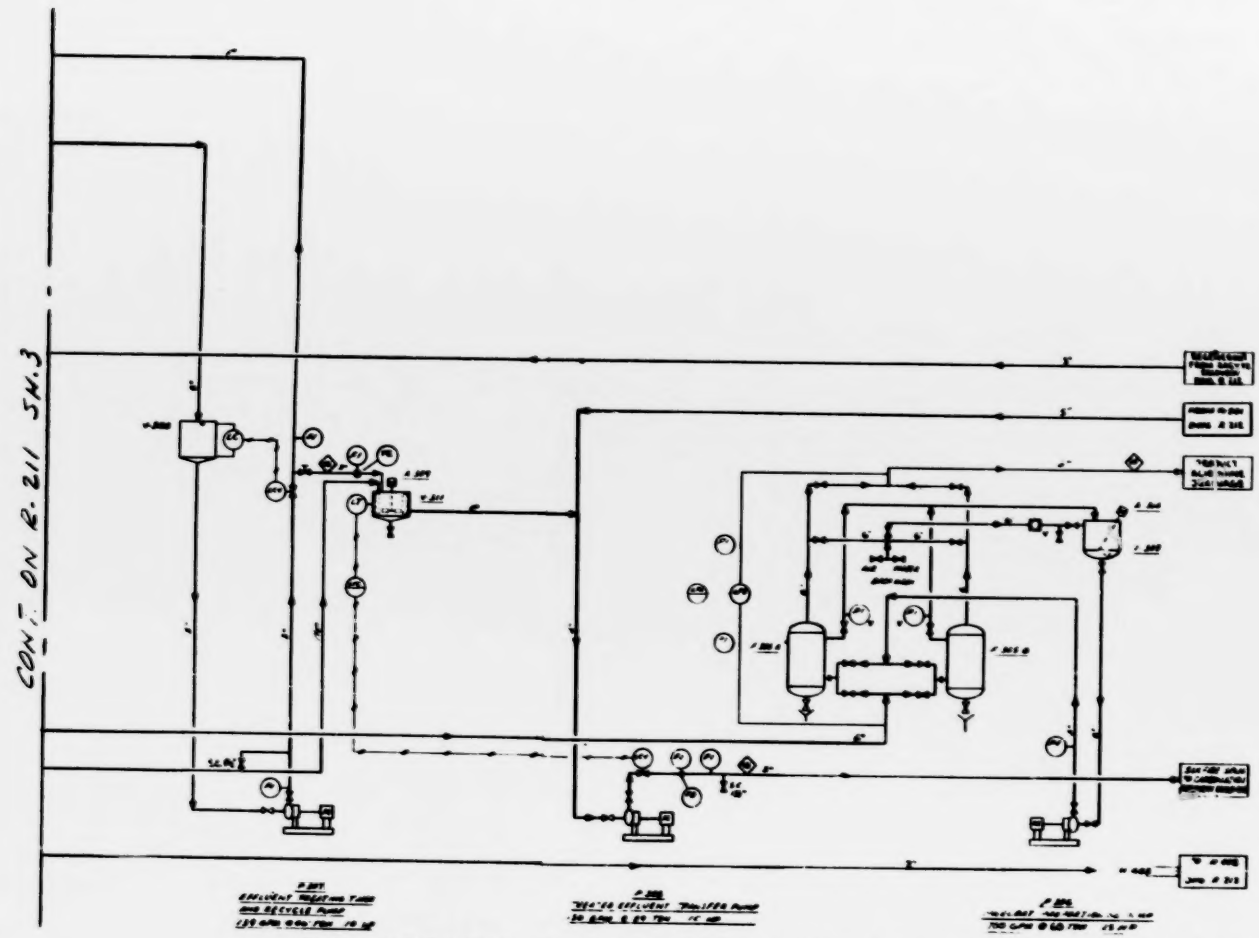
R-211



ENGINEERING DIAGRAM OF A 1 MM GPD PRODUCTION PLANT
FOR NEUTRADESULFATING OF ACID MINE DRAINAGE SHEET 2 OF 4

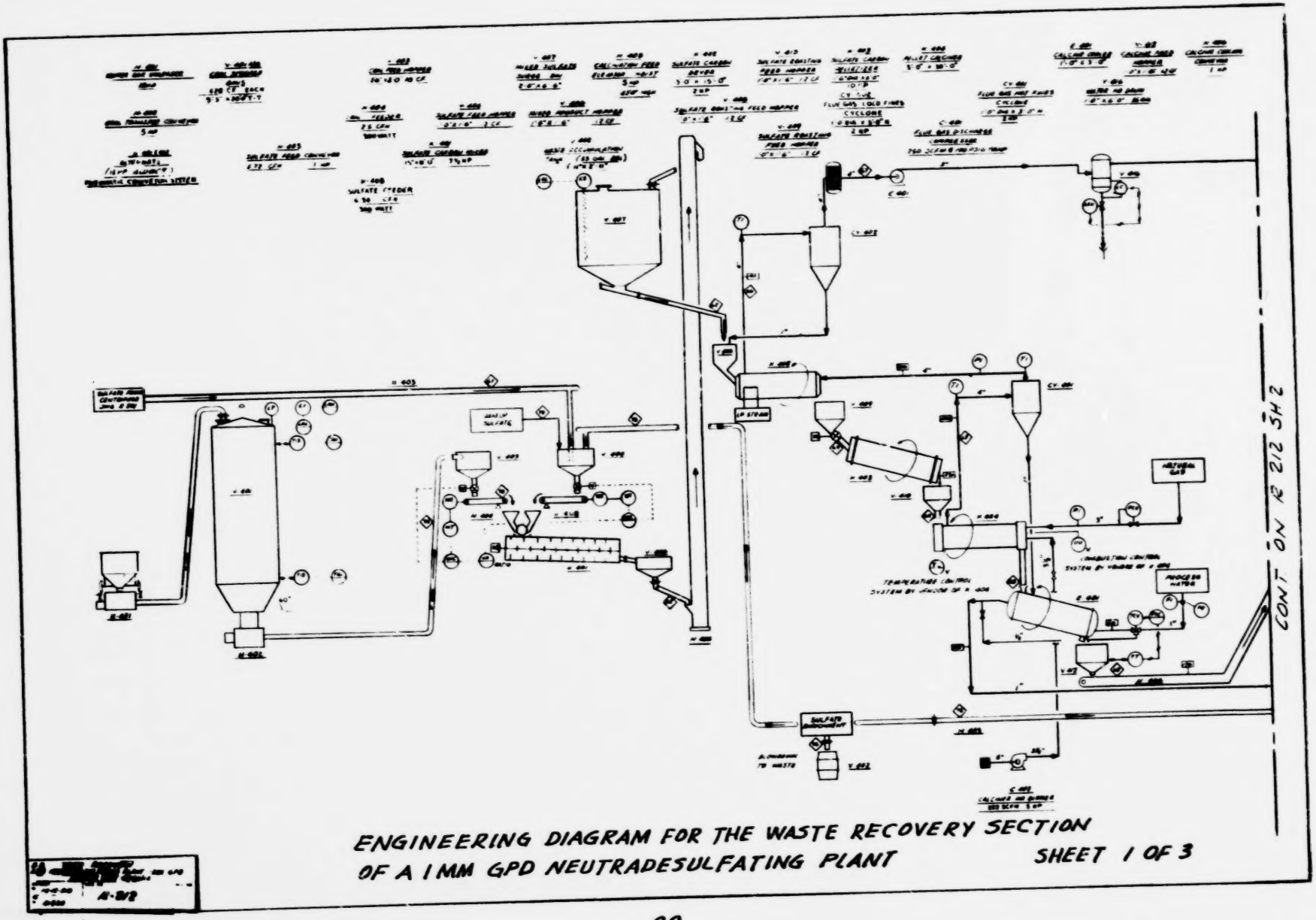


ENGINEERING DIAGRAM OF A 1 MM GPD PRODUCTION PLANT
FOR NEUTRADESULFATING OF ACID MINE DRAINAGE SHEET 3 OF 4



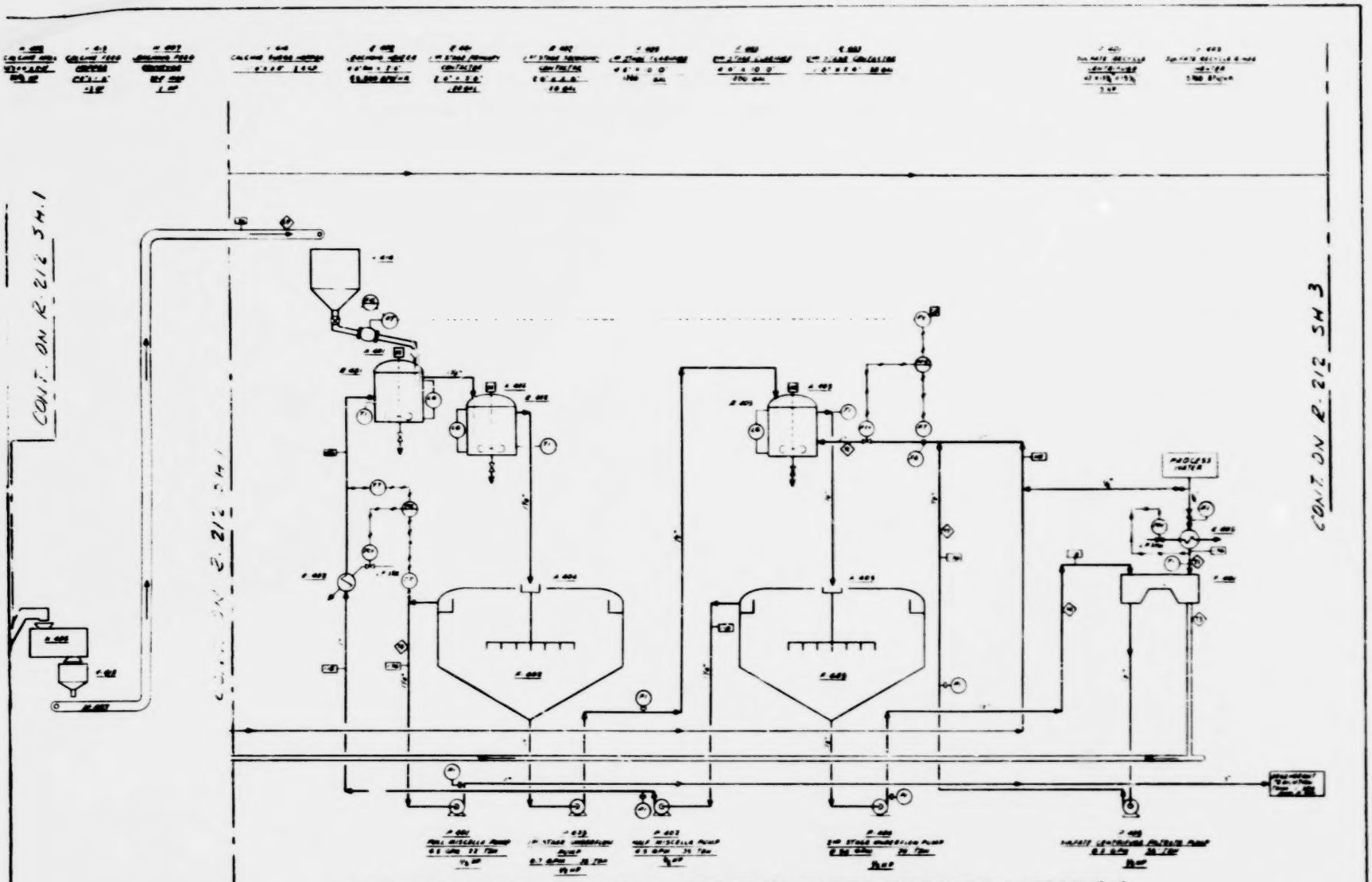
ENGINEERING DIAGRAM OF A 1 MM GPD PRODUCTION PLANT FOR NEUTRADESULFATING OF ACID MINE DRAINAGE

SHEET 4 OF 4

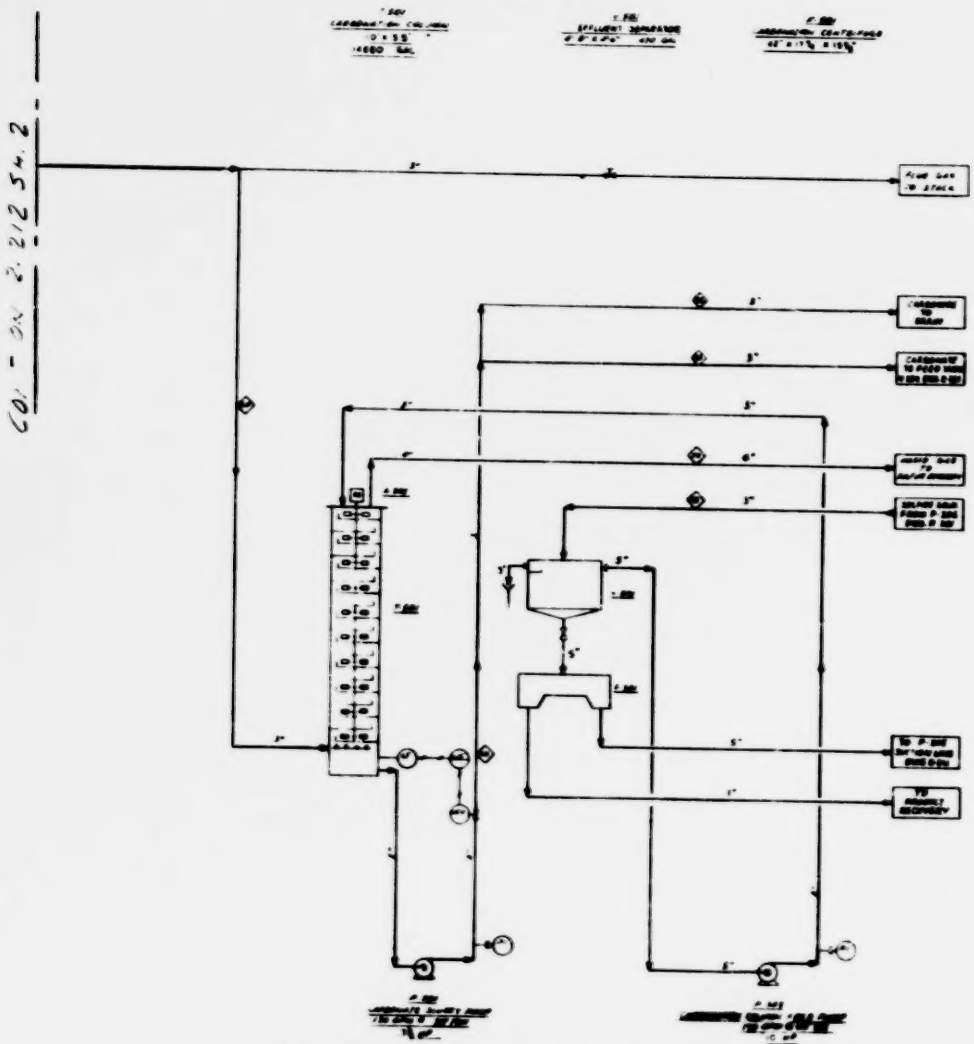


ENGINEERING DIAGRAM FOR THE WASTE RECOVERY SECTION
OF A 1MM GPD NEUTRADESULFATING PLANT

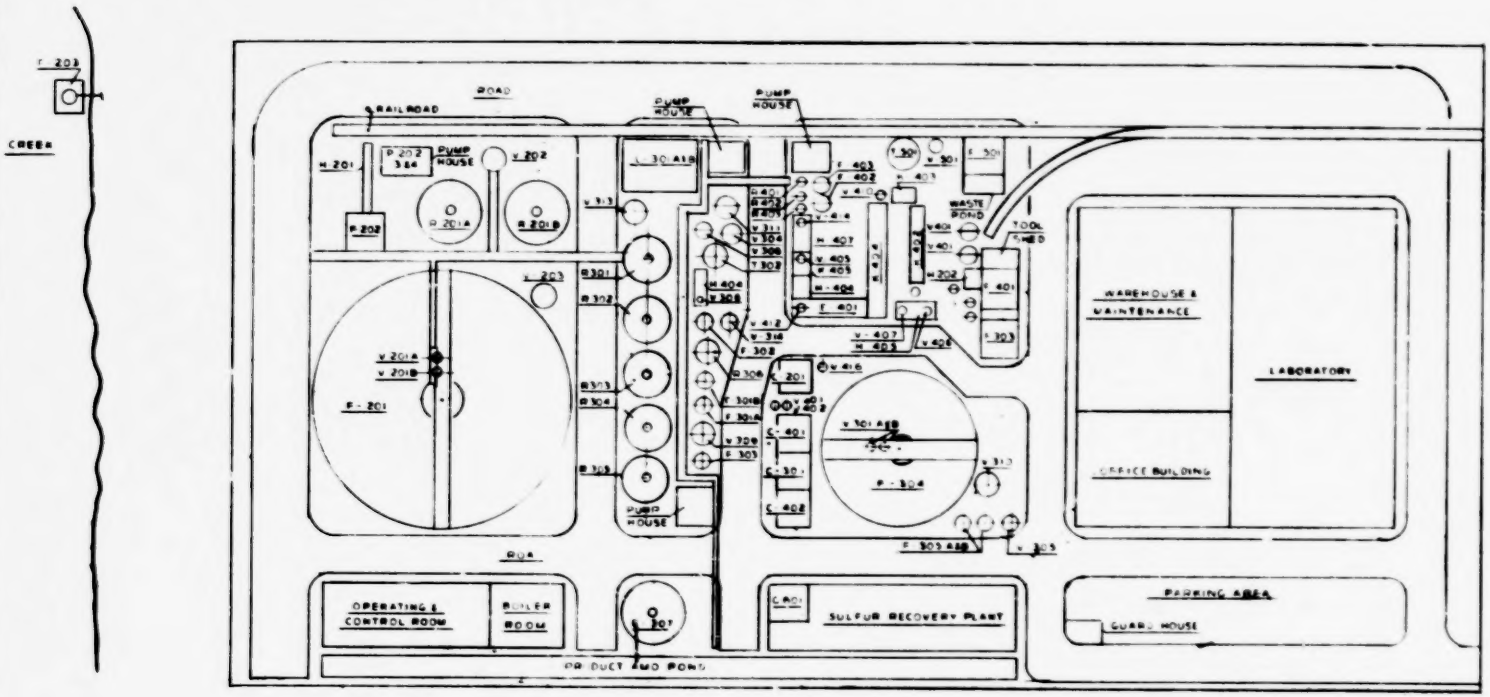
SHEET 1 OF 3



ENGINEERING DIAGRAM FOR THE WASTE RECOVERY SECTION OF A 1 MM GPD NEUTRADESULFATING PLANT SHEET 2 OF 3



ENGINEERING DIAGRAM FOR THE WASTE RECOVERY SECTION OF A 1 MM GPD NEUTRADESULFATING PLANT SHEET 3 OF 3



FEDERAL WATER QUALITY ADMINISTRATION
DEPARTMENT OF THE INTERIOR

CATALYTIC CONSTRUCTION COMPANY

PRELIMINARY PLANT LAYOUT
1 MM GPD PRODUCTION PLANT FOR
NEUTRALIZING OF ACID MINE DRAINAGE

14-12-518 | B-211 | A

41520

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
	05 D	

5 Organization

Catalytic, Inc., Philadelphia, Pennsylvania

6 Title

Neutradesulfating Treatment Process for Acid Mine Drainage

10 Author(s)	16 Project Designation
Engineering Division	14010 DYH
	21 Note

22 Citation

Federal Water Quality Administration, Department of Interior, Report No.

23 Descriptors (Starred First)

* Resins, * Anion Exchange, *Ion Exchange

25 Identifiers (Starred First)

*Barium Elution, *Carbon Dioxide Pressure

27 Abstract

A process has been developed for treatment and removal of major pollutants in surface streams of Appalachia caused by acid mine drainage. The raw water is neutralized with sodium bicarbonate to precipitate iron and aluminum, followed by cation exchange to remove sulfate. Barium is eluted from the exchange resin and reacts with sulfate in the water to form a precipitate. Barium is recovered from the precipitate and is processed to rechange the exchange resin. The water is further treated to remove hydrogen sulfide by conversion to sulfur as a saleable byproduct. The process minimizes the cost of sludge and waste disposal while offering a product water meeting the highest interstate water quality standards. Treatment costs are $2.69 per thousand gallons for a 1 million GPD plant. The project was terminated at the end of Phase I due to the high estimated cost of treatment.

Abstractor	Institution
H.H. Bulkowski	Catalytic, Inc.

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